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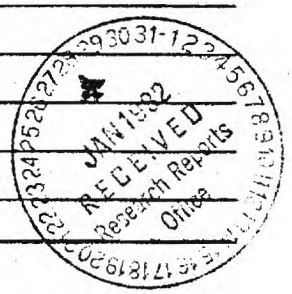
See Attached Gov't Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT if less than $1000; items of $1000 or more must be approved budget or receive prior approval - title will then vest w/GIT, subject to AFOSR right to transfer title within 120 days of completion of Grant.

COMMENTS:

Amend. C adds $64,209 for performance through December 1982. Cum total value of grant: $173,295.



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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 7/6/83

Project Title: Recombination and Chemical Reactions in Dense Ionized Gases

Project No: G-41-629

Project Director: M. R. Flannery

Sponsor: Air Force Office of Scientific Research, Bolling AFB

Effective Termination Date: 12/31/82

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INTERIM TECHNICAL REPORT

RECOMBINATION AND REACTIONS IN DENSE IONIZED GASES

By

M. R. Flannery

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
BOLLING AIR FORCE BASE
WASHINGTON, D. C. 20332

Under

Grant No. AFOSR–80–0055

For Period January 1, 1982 – December 31, 1982

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF PHYSICS
ATLANTA, GEORGIA 30332

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Theoretical research has been conducted on the following two distinct areas of atomic and molecular collisions processes in dense ionized gases:

(a) Ion-Ion Recombination in High Pressure Plasmas
(b) Theory of Rydberg Collisions with electrons, ions and neutrals.

The theory developed for recombination has been applied to the recombination of various combinations of rare gas positive ions (Kr^+, Kr_2^+, Xe^+, Xe_2^+) with negative halides (F^-, Cl^-) in a high pressure background gas (Ne, Ar, Kr,

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Abstract
continued

Xe). The theory formulated and results obtained for (a) and (b) above are fully documented in Appendices A-D of this report.

CONTENTS

Abstract

Theoretical research has been conducted on the following two distinct areas of atomic and molecular collisions processes in dense ionized gases:

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(b) Theory of Rydberg Collisions with electrons, ions and neutrals.

The theory developed for recombination has been applied to the recombination of various combinations of rare gas positive ions (Kr^+, Kr_2^+, Xe^+, Xe_2^+) with negative halides (F^-, Cl^-) in a high pressure background gas (Ne, Ar, Kr, Xe). The theory formulated and results obtained for (a) and (b) above are fully documented in Appendices A-D of this report.

1. Refereed Research Publications under AFOSR Grant

1.1 January 1, 1980 - December 31, 1980

1. "Charge-Transfer in Three-Body Ion-Ion Recombination at Low Gas Densities", Int. J. Quant. Chem.: Quant. Chem. Symp. 14, 477-482 (1980).
2. "Ion-Ion Recombination in $(X^+ + Y^- + X)$ Systems at Low Gas Densities: I. Symmetrical Resonance Charge-Transfer Contribution", J. Phys. B: Atom. Molec. Phys. 13, 3649-3664 (1980).
3. "Three-Body Recombination of Rare-Gas Atomic Ions X^+ with F^- in a Low Density Gas X", with T. P. Yang, J. Chem. Phys. 73, 3239-3245 (1980).
4. "Theoretical Treatment of Collisions of Rydberg Atoms with Neutral Atoms and Molecules. The Semiquantal, Impulse and Multistate-Orbital Theories", Phys. Rev. A 22, 2408-2429 (1980).
5. "Ion-Ion Recombination in $(X^+ + Y^- + Z)$ Systems at Low Gas Densities. II. Elastic Ion-Neutral Collisions", J. Phys. B: Atom. Molec. Phys. 14, 915-934 (1981).

Separate copies of reprints of all of these publications (1) - (5) have already been forwarded during the course of the 1981-year and also were fully documented in the interim report for the previous year (1980).

1.2 January 1, 1981 - December 31, 1981

6. "Thermal Collisions of Rydberg Atoms with Neutrals", J. Phys. B: Atom. Molec. Phys., L657-663 (1980).

7. "Vibrational Deactivation of Oxygen Ions in Low Velocity $O_2^+(X\ ^3\Pi_g$, v=1) + $O_2(X\ ^3\Sigma_g^-$, v=0) Collisions", with T. F. Moran, K. J. McCann, M. Cobb and R. F. Borkman, J. Chem. Phys. 74, 2325-2330 (1981).

8. "Ion-Ion Recombination as a Function of Ion and Gas Densities", Chem. Phys. Letts. 80, 541-546 (1981).

9. "Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation", Phys. Rev. Letts. 47, 163-166 (1981).

10. "Ion-Ion Recombination in Dilute and Dense Plasmas", Int. J. Quant. Chem.: Quant. Chem. Symp. 15, 715-727 (1981).

11. "Theory of Ion-Ion Recombination", Phil. Trans. Roy. Soc. (London) A 304, 447-497 (1982).

12. "Analytical Solutions of the Debye-Smoluchowski Equation for Geminate and Homogeneous Recombination and for Fluorescence Quenching", Phys. Rev. A 25, 3404-3406 (1982).

Reprints of all of the above papers have already been forwarded as informal interim reports during the course of the 1982-year and also were fully documented in the interim report for the previous year (1981).

1.3 January 1, 1982 - December 31, 1982

13. "Ion-Ion Recombination in High Pressure Plasmas", in Applied Atomic Collision Physics, Vol. 3, Gas Lasers (Academic Press, 1982), chapter 5, pages 141-172.

14. "Comment on Exact Closed-Form Solution of the Generalized Debye-Smoluchowski Equation", Phys. Rev. Letts. 49 (1982) 1681.

15. "Comments on Thermal Collisions of Rydberg Atoms with Neutrals", J. Phys. B: At. Molec. Phys. 15 (1982) 3249-3256.

16. "Theory of Rydberg Collisions with Electrons, Ions, and Neutrals", in Rydberg States of Atoms and Molecules (Cambridge University Press, 1982), Chapter 11, pages 393-453.

Copies of all of the above papers #13-16 appear as Appendices A-D, respectively, of this interim report. These papers represent the research work performed during 1982 under the present AFOSR grant.

2. Papers Presented at Scientific Meetings

1. "Basic Microscopic Theory of Chemical Reactions in Dense Gases", Invited Paper delivered to the 3rd Annual Symposium on Atomic and Surface Plasmas, Hintermoos, Austria, February 7-13, 1982.
2. "Theory of Electron-Ion and of Ion-Ion Recombination", Contributed Paper presented to 35th Gaseous Electronics Conference, University of Texas at Dallas, Dallas, October 19-22, 1982.
3. "Basic Microscopic Theory of Ion-Ion Recombination", Contributed Paper presented to 35th Gaseous Electronics Conference, University of Texas at Dallas, Dallas, October 19-22, 1982.
4. "Ion-Ion Recombination in Dense Gases", Invited Paper delivered to International Conference on Lasers '82, New Orleans, La., December 13-17, 1982.

Appendix A

Ion-Ion Recombination in High Pressure Plasmas published in Applied Atomic Collision Physics, Vol. 3, Gas Lasers (Academic Press, 1982) Chapter 5, pages 141-172.

In this Appendix theory suitable for the calculation of the rate α of ion-ion recombination is developed and applied to the processes

$$Kr^+ + F^- + Rg \rightarrow KrF^* + Rg,$$

$$Kr_2^+ + F^- + Rg \rightarrow [Kr_2F] + Rg,$$

$$Xe^+ + Cl^- + Rg \rightarrow XeCl^* + Rg$$

and

$$Xe_2^+ + Cl^- + Rg \rightarrow [Xe_2Cl]^* + Rg$$

as a function of density N of the background gas denoted by Rg ≡ Ne, Ar, Kr and Xe. Also Tables are provided which enable the density dependent rate $\alpha(N)$ to be calculated for the recombination of any rare-gas ion Rg^+(≡ He^+, Ne^+, Ar^+, Kr^+, Xe^+) with F^- or Cl^- in a background gas Rg'(≡ He, Ne, Ar, Kr, and Xe).

All of these results are directly relevant to the kinetics in the development of rare gas-halide lasers pumped by electron beams.

The theory also provides the recombination rate as a function of gas temperature, ion density and time. The main contents are as follows:

I. Recent Theoretical Advances.

II. Recombination as a Function of Gas Density.

III. Basic Microscopic Theory of Ion-Ion Recombination.

IV. Recombination Rates for Various Rare Gas-Halide Systems.

5

Ion–Ion Recombination in High Pressure Plasmas

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Atlanta, Georgia

I. Recent Theoretical Advances

The past few years have witnessed interesting, important, and basic developments in the theory of the ion–ion recombination process,†

$$X^+ + Y^- + Z \longrightarrow [XY] + Z, \tag{1}$$

as a function not only of density of the background gas Z but also of the density of the component ions X^+ and Y^- and of time. Analogous progress in experimental measurement is as yet not forthcoming. Full background and details of the status of ion–ion recombination up to 1976 were given in previous reviews (Flannery, 1976; Bates, 1974a; Mahan, 1973; Flannery, 1972), so that we can concentrate here on essential current development.

† The brackets in Eq. (1) are used to denote that the product may not remain bound.

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Recent theoretical treatments have considered the effectively exact limit of the recombination coefficient α at low gas densities (Bates and Moffett, 1966; Bates and Flannery, 1968; Flannery, 1980, 1981a; Flannery and Yang, 1980) and its extension (Bates and Mendaš, 1980a) from this linear three-body (Thomson, 1924) region into the nonlinear gas density regime, with the aim (Bates and Flannery, 1969) of eventual connection to the high density Langevin–Harper region (Bates, 1975) in which the macroscopic effects of mobility and diffusion control events. Since the key theoretical problem is complex and difficult and since various phenomenological approaches tended to mask the essential theoretical considerations, it is only recently that a basic theory providing theoretical foundation and the low density–high density link has been developed (Flannery, 1982a) purely from microscopic principles. Macroscopic effects—recombination sink, mobility, diffusion—are truly addressed in language of their microscopic origins and follow quite naturally from this theory, which provides α as a general function of gas density N, of ion density $N^{\pm}$, and of time t.

In the meantime, resort has been made to procedures (Flannery, 1978; Flannery and Yang, 1978, a–c; Wadehra and Bardsley, 1978) that are essentially modifications of the approach of Natanson (1959), who, via generalization of a method of Fuks (1958) on evaporation of water droplets in a gaseous medium, provided some insight into the link between low and high gas densities N. All of these approaches based on a strong collision trapping radius remain phenomenological in the spirit of the approaches of Langevin (1903), Harper (1932), and Thomson (1924), the original pioneers of the subject.

Resort has also been made to very effective Monte Carlo (MC) computer simulations (Bates and Mendaš, 1978b; Bates, 1980a,b; Bardsley and Wadehra, 1980), which, although they produce numerical α, do not deepen theoretical understanding of the basic issues involved. However, from their MC work, Bates and Mendaš (1978b) discovered the enhancement of mutual neutralization ($X^+ + Y^- \rightarrow X^* + Y$) as the gas density N is raised, an important effect theoretically explained later by Bates (1979). Feibelman (1965) had earlier adopted MC procedures for the low density limit to α, but the criteria for stabilization of recombination was based on the completion of a certain number (~ 10) of ion–neutral collisions, rather than on collisional deactivation of an ion pair below a certain negative energy level.

An important advance has been made by Bates (1980a–c), who inferred from dimensional considerations the existence of a universal curve for α covering any gas temperature, any combination of the masses and of interaction constants for any recombination system, a powerful theorem confirmed by his MC work.

The preceding recent activity has been largely prompted by the continuing classical nature of the problem and, in some certain measure, by the key role (cf. Flannery, 1979, also Chapters 3 and 10) of ion–ion recombination in populating the upper molecular electronic states of rare-gas halide lasers that operate not only at high gas pressures ($\sim\frac{1}{2}$–10 atm) but also at moderately high ion densities $N^{\pm} \sim 10^{12}$–10^{14} cm^{-3}. Reliable laboratory experiments even at low $N^{\pm} \sim 10^{8}$ cm^{-3} but high N are difficult since identity of the ions changes as N is raised. All the preceding theoretical treatments and any available measurements (Section IV) pertain tacitly to dilute ionization ($N^{\pm} \sim 10^{8}$ cm^{-3}), except the basic microscopic general development (Flannery, 1982a). This treatment illustrates how the ion–ion interaction $V(R)$, which no longer can be assumed ab initio to be pure Coulomb, is coupled via Poisson's equation to the ion number densities in turn coupled directly and via V both to the (compressible) recombination kinetic sink and to the (incompressible) streaming terms basic to diffusion and mobility effects. The recombination coefficient α as a function of N and of $N^{\pm}$ is then determined by the self-consistent phase space densities (which generates the consistent V) and by the microscopic collisional rates for energy-change transitions in an ion pair.

Bates (1981a) has reasoned that the straightforward use of the Debye–Hückel (DH) interaction, as in Morgan *et al.* (1980), is defective and that the Langevin result (Section II) is the correct limit at high N for all $N^{\pm}$. The DH interaction allows for plasma sheathing only under equilibrium conditions, as in the limit of vanishing N (Flannery, 1981b, 1982a, Section III) and of course when $V \ll kT$. As N increases, use of an interaction self-consistent with the number densities is the proper procedure (Section III).

II. Recombination as a Function of Gas Density

A. Low and High Gas Density Limits

In the limit of high gas densities N, the mean free paths λ_i of the positive and negative ions i ($\equiv 1, 2$) are vanishingly small and the frequency of ion–neutral collisions is sufficiently high that the diffusional drift ion–ion speed v is in equilibrium with the electrostatic field and that the rate of reaction between the positive and negative ions $i(\equiv 1, 2)$ in the gas 3 is instantaneous in comparison with the rate of transport of the ions. The recombination rate is therefore limited by the rate of relative transport of 1 and 2 to separation R at which reaction occurs. Langevin (1903) attributed transport solely

to ion–ion drift under their mutual Coulombic field V at a rate

$$\alpha_K = 4\pi R^2 |-\nabla V/e| K = 4\pi K e, \tag{2a}$$

where the mobility K for (1–2) relative motion, the sum of the individual mobilities of each ion in the gas, varies as N^{-1}. Harper (1932) attributed transport solely to diffusion at rate

$$\alpha_D = 4\pi D R, \tag{2b}$$

which, via use of the Einstein relation $De = KkT$ between K and the coefficient D for relative diffusion, reduces to (2a) only at $R = (e^2/kT)$. Bates (1975) combined diffusion and drift to obtain the full transport rate

$$\alpha_{TR} = 4\pi K e/[1 - \exp(-e^2/RkT)] \to \alpha_K, \tag{2c}$$

which tends to (2a) for $R \ll R_e = (e^2/kT)$, appropriate to high N. For a general interaction $V(R)$ the diffusional-drift transport rate is

$$\alpha_{TR} = 4\pi D\tilde{R}, \qquad \tilde{R} = \left[\int_R^\infty \exp(KV/De) R^{-2}\, dR\right]^{-1}, \tag{2d}$$

which shows that drift under V is acknowledged in the Harper rate (2b) simply by replacing R by $\tilde{R}$. Also the Langevin method underlying (2a) is deficient in the sense that for the limit of small R it reproduces the correct constant limit of the full transport rate only for a pure Coulomb interaction and yields a divergent limit for all other long-range attractions (see Section III.B).

At low N, ion–neutral collision frequencies $(\langle v\rangle/\lambda_i)$ are vanishingly small so that the relative (1–2) approach speed v becomes higher than thermal and a large fraction of close (1–2) encounters do not yield neutralization. Assuming that recombination results via a single strong (ion i–neutral 3) collision within some trapping radius R_T centered at the other ion, then α increases linearly with N as

$$\alpha_{low} = K_{eq}(R_T)[\langle v\rangle/\lambda_1 + \langle v\rangle/\lambda_2] \equiv \tfrac{4}{3}\pi R_T^3 N \sigma_D \langle v\rangle, \tag{3}$$

where K_{eq} is the equilibrium constant $(\frac{4}{3}\pi R_T^3)$ averaged over all ion–ion energies for formation of R ion pairs with internal separations $R \leqslant R_T$ and where σ_D is the sum of the momentum-change cross sections for each (i–3) encounter. For a suitable choice $(\frac{2}{3}\, e^2/kT)$ for R_T, (3) is identical with the low gas density limit of Thomson (1924). Bates and Moffett (1966) and Bates and Flannery (1968) developed the first rigorous theoretical account of low density recombination based on microscopic energy-change prin-

ciples, established via quasiequilibrium kinetics the essential development in internal energy of recombining ion pairs, and placed the low density limit that exhibits the same linear N dependence as (3) on firm theoretical grounds. This work has been expanded (Flannery, 1980, 1981a) and exact low density limits [normalized to Thomson's result (3)] have been provided for an extensive range of ion and neutral masses.

As N is raised, the ion sink represented by (3) increases to such an extent that its effect on the number density $N_i(R)$ of R ion becomes important and must be coupled to the solution of N_i via some equation expressing diffusional drift, which decreases the survival rate of approaching ions, thereby resulting in an overall increase of α with N less than linear and in eventual decrease; i.e., the reaction rate is increasing, becomes comparable to and is eventually faster than the transport rate as N is increased. In contrast, Thomson (1924) assumed as N is raised that the probability $P(R_T/\lambda_i)$ of effective ion–neutral collisions for ion pairs with $R \leqslant R_T$ eventually increased to unity as

$$P(X) = W(X_1) + W(X_2) - W(X_1)W(X_2), \qquad X_i = (R_T/\lambda_i), \tag{4}$$

where the probability for individual ion–neutral collisions (for a straight line ion–ion trajectory) is

$$\begin{aligned} W(X) &= 1 - (1/2X^2)[1 - \exp(-2X)(1 + 2X)] \\ &\to \begin{cases} \frac{4}{3}X(1 - \frac{3}{4}X + \frac{2}{5}X^2 - \frac{1}{6}X^3 + \cdots), & \text{low } N, \\ 1, & \text{high } N, \end{cases} \end{aligned} \tag{5}$$

which yields (3) as $N \to 0$ but which is defective at high N. Bates and Mendaš (1978b) extended the microscopic quasiequilibrium treatment into the nonlinear N region by rigorously including the decrease in the number of *effective* ion–neutral collisions in an increasingly dense medium, and obtained a nonlinear increase in α consistent with the initial nonlinear ascent exhibited by (5). The Thomson rate (3) is essentially the reaction rate.

The failure of the Thomson model at high N is due both to the neglect (Flannery, 1982a) of the decreasing effect of accelerations produced by the ion–ion field between frequent ion–neutral collisions, a mobility effect required for thermodynamic equilibrium in the absence of sources and sinks and to the explicit neglect of diffusion of the ions before entering the reaction R_T sphere, although the role of diffusion in the energy-change reaction is implicit in (5). Both effects that originate with the transport of ions in phase space are a natural consequence of the basic theory (Flannery, 1981c, 1982a) outlined in Section III.

B. Intermediate Gas Densities

Two procedures based on the use of the exact quasiequilibrium low density limits and the exact high density limits within either a treatment based on ion transport followed by a finite rate of reaction (Flannery, 1982a) or the Bates–Universal curve are now discussed and are recommended for evaluation of α versus gas density N, in general. The basic theory (Flannery, 1982a) shows that the recombination coefficient α can be written exactly as (Section III)

$$\alpha = \alpha_{RN}\alpha_{TR}/(\alpha_{RN} + \alpha_{TR}), \tag{6}$$

where α_{RN} and α_{TR} are the reaction and transport rates, respectively, associated with microscopic three-body collisions and with diffusional drift. At low gas densities N, $\alpha \to \alpha_{RN}$, the rate-limiting step of transport reaction, and the ions are in a quasi-Boltzmann equilibrium. At high N, $\alpha \to \alpha_{TR}$, the rate-limiting step, and the ion distribution departs substantially from Boltzmann. The basic theory therefore established a firm theoretical basis of a relationship (6) that is intrinsic (Bates and Flannery, 1969) to the expression of Natanson (1959) for α and that exhibits striking similarity to electrical networks (Bates, 1974b).

1. *Reaction and Transport Rates*

The rate for recombination of ions is the rate of reaction α_{RN}, provided a Boltzmann distribution of ions is maintained (Flannery, 1982a) as at low gas densities. Assume reaction occurs by a strong collision with the gas of each ion ($i = 1, 2$) of an ion pair with internal separation $\lesssim R_i$. Then, for ions with mean free paths λ_i in the gas,

$$\alpha_{RN} = \pi[R_1^2 W(X_1)C_1E_1 + R_2^2 W(X_2)C_2E_2 - R_S^2 W(Y_1)W(Y_2)G]\langle v_{12}\rangle, \tag{7}$$

where $\langle v_{12}\rangle$ is some averaged ion–ion speed of approach, X_i is R_i/λ_i, and Y_i is R_S/λ_i in terms of the minimum value R_S of R_1 and R_2. The focusing factor

$$C_i = \left[1 + \frac{2}{3kT}\int_{R_i}^{(R_i+\lambda_i)}\left(\frac{\partial V}{\partial R}\right)dR\right] \equiv 1 + \delta_i^{-1}, \qquad i = 1, 2 \tag{8}$$

acknowledges ion–ion trajectories under $V(R)$ rather than straight line paths implicit in (5) for the ion–neutral collision probability W, and

$$E_i = \exp[-V(R_i + \lambda_i)/kT] \xrightarrow{V \to -e^2/R} \exp(3R_i/2\delta_i\lambda_i) \tag{9}$$

acknowledges the Boltzmann enhancement in the ion number density due to the field at $(R_i + \lambda_i)$ at which the last (ineffective) ion–neutral collision occurs just before the ion enters the recombination sink within R_i. If the

speed intrinsic in (8) is taken as its mean value rather than its rms value as here, then C_i is $(1 + 3/2\delta_i)$. The probability of simultaneous collisions within R_S is $W(Y_1)W(Y_2)$ and simple geometric arguments show that the factor G in (7) is either C_1E_1 or C_2E_2, depending on whether R_S is R_1 or R_2, respectively. The initial kinetic energy of (1, 2) relative motion is

$$T_i = \tfrac{3}{2}kT + \int_R^{(R+\lambda_i)} \left(\frac{\partial V}{\partial R}\right) dR, \tag{10}$$

since the ions on average are uninterrupted by collision only for (1, 2) separations between $(R + \lambda_i)$ and R. Ion pairs on collision with a neutral become incapable of expanding outward from R to $(R + \lambda_i)$, provided their final internal kinetic energy T_f is just insufficient to overcome the force of ion–ion attraction effective between collisions of mean free path, i.e., when

$$T_f \leqslant \int_R^{(R+\lambda_i)} \left(\frac{\partial V}{\partial R}\right) dR, \tag{11}$$

which reduces to Thomson's condition when $\lambda \to \infty$ in the limit of vanishing N. The collision parameter δ_i is such that the change $(T_i - T_f)$ is δT_f. The criteria (11) for a pure Coulomb attraction then yields trapping radii,

$$R_i = \tfrac{1}{2}\lambda_i\{[1 + 4\delta_i R_T/\lambda_i]^{1/2} - 1\} \to \begin{cases} \delta_i R_T & \text{as} \quad N \to 0, \\ (\delta_i R_T \lambda_i)^{1/2} & \text{as} \quad N \to \infty, \end{cases} \tag{12}$$

which decrease monotonically with λ_i and which satisfy $R_i(R_i + \lambda_i) = \delta_i \lambda_i R_T$. The Thomson radius R_T is $(2e^2/3kT)$. Note that, within R_i of significance to the recombination process, the ion–ion interaction V is $\gtrsim kT$ such that as $N^{\pm}$ is raised, linearization ($\equiv V \ll kT$) of Poisson's equation (Section III.C) for solution of V is *not* valid, except at asymptotic R of little significance to reaction. The low density limit to R_i is $\delta_i R_T$ such that the recombination coefficient (7) tends to the zero-density limit,

$$\alpha_L \equiv \alpha_{L1} + \alpha_{L2} = C_1\delta_1^3\alpha_{T1} + C_2\delta_2^3\alpha_{T2}, \tag{13}$$

where

$$\alpha_{Ti} = \tfrac{4}{3}\pi R_T^3 \langle v_{12} \rangle / \lambda_i \tag{14}$$

is the Thomson partial recombination coefficient as $N \to 0$. Hence from knowledge of the ratio $\mathscr{R}_{Ti}$ of the exact low density quasiequilibrium limits of α_{Li} to α_{Ti}, the collision parameter δ_i is obtained from solution of

$$\delta_i^3 + \delta_i^2 - \mathscr{R}_{Ti} = 0 \tag{15}$$

for various systems of interest. Hence α_{RN} in (6) can be determined directly from (7)–(9), (12), and (15). In previous papers (Flannery and Yang, 1978a–c)

an expression for δ_i based on classical mechanics and depending on the masses M_i of the ions (i = 1, 2) and neutral gas (i = 3) was derived and used (compare with Wadehra and Bardsley, 1978). The ratio $\mathscr{R}_{Ti}$ has now been provided (Flannery, 1980, 1981a) from the exact quasiequilibrium treatment as a function of masses of the species involved for the respective cases of

$$X^+ + Y^- + Z \longrightarrow [XY] + Z, \tag{16}$$

where energy-change transitions occur via elastic ion–neutral collisions, and of

$$X^+ + Y^- + X \longrightarrow [XY] + X, \tag{17}$$

where, in addition to the elastic (Y^-–X) encounter, a symmetrical resonance charge transfer encounter (X^+–X) also occurs. The relative importance of each of these types of encounter has been illustrated (Flannery, 1981a). Tables I and II display δ_i resulting from (15) for all rare-gas (He^+, Ne^+, Ar^+, Kr^+, Xr^+) halide (F^-, Cl^-) combinations in a like or unlike gas of current interest.

Since the recombination rate at high gas densities is limited by ion transport alone in the presence of an instantaneous reaction sink, then (Bates, 1975; Flannery, 1982a)

$$\alpha_{high} = \alpha_{TR} = 4\pi[D_1\tilde{S}_1 + D_2\tilde{S}_2], \quad \tilde{S}_i = \left[\int_{R_i}^{\infty} \exp(KV/De)R^{-2}\,dR\right]^{-1}, \tag{18}$$

TABLE I

Collision Parameters ($10\delta_i$) to Be Used in (7) and (18) for [(R^+–F^-) + M] Recombination Systems[a]

M		(He^+–F^-)	(Ne^+–F^-)	(Ar^+–F^-)	(Kr^+–F^-)	(Xe^+–F^-)
He	δ_1	6.7426*	5.3325	3.8215	2.3291	1.5719
	δ_2	2.9225	5.5468	6.4206	7.0552	7.3018
Ne	δ_1	6.4214	5.5105*	4.6390	3.0945	2.2555
	δ_2	3.4644	6.0276	6.7437	7.1975	7.3531
Ar	δ_1	6.0852	5.8746	4.5694*	3.3621	2.5172
	δ_2	3.5779	6.0119	6.6016	6.9052	6.9767
Kr	δ_1	5.8323	5.8264	4.9094	3.4300*	2.7526
	δ_2	3.6444	5.9422	6.3935	6.4993	6.4554
Xe	δ_1	5.7320	5.7923	4.9311	3.6565	2.7704*
	δ_2	3.6668	5.8987	6.2758	6.2710	6.1497

[a] Those appropriate to symmetrical resonance charge transfer are indicated by asterisks (*).

TABLE II

As in Table I Except for $[(R^+-Cl^-) + M]$ Recombination Systems[a]

M	(He^+-Cl^-)	(Ne^+-Cl^-)	(Ar^+-Cl^-)	(Kr^+-Cl^-)	(Xe^+-Cl^-)
He	6.9163*	6.1839	4.8025	3.1711	2.3296
	1.8370	4.1860	5.2366	6.1421	6.5378
Ne	6.3101	6.1565*	5.6520	4.1242	3.1580
	2.3706	4.9808	6.0250	6.8585	7.2000
Ar	5.8121	6.4924	5.4374*	4.4182	3.4771
	2.5271	5.1305	6.1033	6.8261	7.0991
Kr	5.4095	6.3254	5.7998	4.3916*	3.7465
	2.6375	5.1910	6.0658	6.6325	6.8039
Xe	5.2414	6.2311	5.7773	4.6939	3.6985*
	2.6800	5.1986	6.0168	6.4888	6.5829

[a] Those appropriate to symmetrical resonance charge transfer are indicated by asterisks (*).

where K_i and D_i, the mobility and diffusion coefficient, respectively, of each ion in the gas are related by $D_i e = K_i kT$. For Coulombic attraction with natural unit $R_e = e^2/kT$, $\tilde{S}_i$ reduces to $R_e[1 - \exp(-R_e/R_i)]^{-1}$, which tends to R_e at large N since $R_i \to (\delta_i R_T \lambda_i)^{1/2} \ll R_e$, and (18) tends to the Langevin–Harper result. The overall recombination rate α for all gas densities N can then be obtained from (6), which is controlled by the limiting rate α_{RN} and α_{TR} at low and high N, respectively. Illustrations of α versus N so obtained with the aid of Tables I and II are best deferred until Section IV.

2. *Bates's Universal Plot*

Bates (1980b) has recently presented a procedure by which α_x versus N_x for some unknown case labeled X may be deduced from a plot of α_s versus N_s for some standard case S. Bates (1980a) has carried out the most extensive Monte Carlo simulations for the $[(O_4^+ - O_4^-) + O_2]$ system, which he therefore takes as the standard case, and which incidentally is the only case for which reasonably accurate measurements (McGowan, 1965) up to 1 atm gas pressure of a relatively simple system are available. Since the low and high density limits (3) and (2) vary with N as

$$\alpha_{low} = AN, \qquad \alpha_{high} = B/N, \tag{19}$$

where A and B are constants peculiar to the recombination system, then by attaching subscripts x and s to quantities appropriate to the unknown and

standard cases, Bates (1980b) inferred from dimensional considerations that scaling parameters

$$\lambda = (A_s B_s / A_x B_x)^{1/2}, \qquad \eta = (A_x B_s / A_s B_x)^{1/2} \tag{20}$$

are such that a plot of $\lambda(T/300)^{3/2}\alpha_x$ versus $\eta(300/T)^t N_x$ is a universal curve. The temperature universality is also included where the index t is 1 or $(\frac{3}{2})$ for a hard-sphere or pure-polarization ion–neutral interaction, respectively (Bates, 1980c). This is a powerful theorem that only requires knowledge of a given case S, together with the appropriate low and high density limits for the $\bar{s}$ and $\bar{x}$ cases, which are accurately given, respectively, by the effectively exact quasiequilibrium constant gradient (Bates and Flannery, 1968; Flannery, 1980, 1981a) as $N \to 0$ and by the measured mobilities. The theorem is exact under certain conditions, and various procedures to acknowledge effects of mass asymmetry are recommended by Bates (1980b). Results are illustrated in Section IV.

III. Basic Microscopic Theory of Recombination

A. Function of Gas Density

A full basic theory of ion–ion recombination was recently developed (Flannery, 1982a) as a function of gas density N, of ion density $N^{\pm}$, and of time t. The reader is referred to the original paper since only a brief outline of the key equations is presented here. Let $n_i(\mathbf{R}, \mathbf{v}_i, t)$ be the phase density of negative ions moving with velocity $\mathbf{v}_i$ at separation $\mathbf{R}$ from a stationary positive ion. The interaction between the positive and negative ions is $V(R)$ such that the negative ions with reduced mass m can be viewed as moving through the gas Z under an external field of intensity $\mathbf{E} = -\nabla V$ in the reference frame of stationary positive ions. The *Boltzmann equation* for the phase density is therefore

$$\frac{dn_i}{dt}(\mathbf{R}, \mathbf{v}_i, t) \equiv \frac{\partial n_i}{\partial t}(\mathbf{R}, \mathbf{v}_i, t) + \mathbf{v}_i \cdot [\nabla_{\mathbf{R}} n_i(\mathbf{R}, \mathbf{v}_i, t)] + \left(\frac{e\mathbf{E}}{m}\right) \cdot \nabla_{\mathbf{v}_i} n_i(\mathbf{R}, \mathbf{v}_i, t)$$
$$= \left[\frac{\partial n_i}{\partial t}\right]_{el} - \left[\frac{\partial n_i}{\partial t}\right]_{s} \tag{21a}$$

in terms of the continuous incompressible (diffusional-drift) *streaming* terms on the left-hand side and of the discontinuous *collisional* terms written as

$$\left[\frac{\partial n_i}{\partial t}\right]_{el} = N\left[\sum_{f=-V(R)}^{C} n_f(\mathbf{R}, E_f, t) k_{fi}(R) - n_i(\mathbf{R}, E_i, t) \sum_{f=-V(R)}^{C} k_{if}(R)\right], \tag{21b}$$

the term for *elastic* collisions of individual positive and negative ions with the gas species, and as

$$\left[\frac{\partial n_i}{\partial t}\right]_S = N \sum_{f=-V(R)}^{-M} n_f(\mathbf{R}, E_f, t) k_{fi}(R), \tag{21c}$$

the *sink* term. The number density $N_i^* dR$ of ion pairs with internal separation between R and $R + dR$ and with internal velocity $\mathbf{v}_i$ in the interval $d\mathbf{v}_i$ about $\mathbf{v}_i$ is $4\pi R^2 N^+ n_i \, dR \, d\mathbf{v}_i$.

Elastic binary collisions of each member of an ion pair of fixed internal separation R with gas atoms produce changes in E_i, the internal energy, $\frac{1}{2}mv_i^2 + V(R)$, of each R_i ion pair. The rate for such inelastic transitions is $k_{if}(R)\,\mathrm{cm}^3/\mathrm{s}$ such that Nk_{if} is the frequency of energy conversion of R_i ion pairs to R_f ion pairs. Thus (21b) is the net rate of collisional production of R_i ion pairs from all R_f pairs with energy levels f between the far continuum C and the lowest level $-V(R)$ consistent with separation R. When the recombination sink is in effect, (21b) oversubscribes the effect of collisions by the amount (21c) in which $-M$ denotes the bound level given by the upper level of $-V$ and $-E_s$, which is the energy level below which recombination is assumed to be stabilized, i.e., no upward transitions out of the range $[-V, -M]$ can occur. The "elastic" first part of (21b) of the collision term, in contrast to the streaming terms in the left-hand side of (21a) attempts to drive the momentum-space part of the distribution towards Maxwellian at a given R, while the sink part causes a redistribution in internal energies E_i of the ion pairs, such that (R, E_i) variables provide the set more natural for expression of the sink, rather than the set (R, v_i), which is natural for thermodynamic equilibrium. The energy continuum corresponding to unbound ion pairs is denoted by C (which then implies an integration over the continuum rather than a summation over bound states); for a quasicontinuous spectrum of internal energies (valid for heavy particles) the f summation in (21b) and (21c) can be replaced by the corresponding integral. Expressions for the energy-change rates k_{if} have been derived for various classes of interaction in ion–neutral scattering: general ion–neutral elastic scattering (Bates and Flannery, 1968), hard-sphere scattering (Flannery, 1981a), hard-sphere repulsion plus polarization attraction (Bates and Flannery, 1968; Flannery, 1968), and symmetrical resonance charge transfer (Bates and Moffett (1966) for $[X^+–X^-]$ in X and Flannery (1980) for $[X^+–Y^-]$ in X or Y).

The present theory therefore permits the full evolution of the phase-space ion densities by effective and ineffective† microscopic collisions, by inward and outward diffusion due, respectively, to the presence of the

† In the sense of promoting recombination or thermodynamic equilibrium, respectively.

recombination sink (at small and intermediate R) and to the outward reaction to inward mobility (at larger R), and by the accelerations produced by mutual electrostatic ion fields *between* ion neutral collisions in an increasingly dense medium.

From the equations of *continuity* and *momentum* derived (Flannery, 1982a) for ion–ion recombination from the Boltzmann equation (21), the configuration space density

$$n^-(\mathbf{R},t) = \int n_i(\mathbf{R},\mathbf{v}_i,t)\,d\mathbf{v}_i \tag{22}$$

is given by the solution of

$$-\frac{\partial n^-}{\partial t}(\mathbf{R},t) + \nabla\cdot\mathbf{J}_i = \int\left[\frac{\partial n_i}{\partial t}(\mathbf{R},\mathbf{v}_i,t)\right]_S d\mathbf{v}_i \equiv \sum_{i=-V(R)}^{C}\left[\frac{\partial n_i}{\partial t}(\mathbf{R},E_i,t)\right]_S, \tag{23}$$

where the diffusional drift current, obtained from the momentum equation under certain criteria (Flannery, 1982a) associated with chemical reactions, is

$$\begin{aligned}\mathbf{J} = -\mathbf{J}_i &= -D\nabla n^-(\mathbf{R},t) + (K/e)n^-(\mathbf{R},t)\nabla V(R)\\ &\equiv -D\exp(-V/kT)\nabla[n^-(\mathbf{R},t)\exp(V/kT)].\end{aligned} \tag{24}$$

The temperature T is introduced above via the Einstein relation ($De = KkT$) between the coefficient D for relative diffusion and the relative mobility K.

The sink term for spherically symmetric n_i

$$\sum_{i=-V}^{C}\left[\frac{\partial n_i}{\partial t}\right]_S = N\sum_{i=-V}^{C}\left[n_i(R,E_i,t)\sum_{f=-V}^{C}k_{if}(R) - \sum_{f=-M}^{C}n_f(R,E_f,t)k_{fi}(R)\right] \tag{25a}$$

effectively behaves as (Flannery, 1982a)

$$\sum_{i=-V}^{C}\left[\frac{\partial n_i}{\partial t}\right]_S = N\sum_{i=-E}^{C}\left[n_i(R,E_i,t)\sum_{f=-V}^{-E}k_{if}(R) - \sum_{f=-M}^{-E}n_f(R,E_f,t)k_{fi}(R)\right], \tag{25b}$$

which is the net downflow of R ion pairs past some negative energy level $-E$ below which collisional quasiequilibrium

$$n_i(R,E_i,t)\sum_{f=-V}^{C}k_{if}(R) = \sum_{f=-M}^{C}n_f(R,E_f,t)k_{fi}(R), \qquad i \leqslant E \tag{26}$$

is assumed to exist at each R. Since R remains fixed during an ion–neutral collision, k_{if} and the sink term (25b) are therefore effective only for $R \leqslant R_E$,

the maximum turning point appropriate to the bound level $-E$. Thus

$$-\frac{\partial}{\partial t}\int_0^R 4\pi R^2 n^-(R,t)\,dR + 4\pi R^2 J_i(R,t) = \alpha_3(R)n^-(R,t) \xrightarrow{R \geqslant R_E} \alpha N^-, \tag{27}$$

where the frequency of loss of all ion pairs with internal separations $\leqslant R$ is

$$\alpha_3(R)n^-(R,t) = N\int_0^R 4\pi R^2 \sum_{i=-E}^{C}\left[n_i(R,E_i,t)\sum_{f=-V}^{-E} k_{if}(R) - \sum_{f=-M}^{-E} n_f(R,E_f,t)k_{fi}(R)\right], \tag{28}$$

which is constant for $R \geqslant R_E$ and which defines α_3 to be an averaged rate of reaction within R appropriate to the local ion density at R. If F_∞ is the frequency of production of negative ions at an infinite distance from the positive ions, then

$$\frac{\partial}{\partial t}\int_0^\infty 4\pi R^2 n^-(R,t)\,dR = F_\infty - \alpha N^- \tag{29}$$

and steady state conditions can be maintained by setting $F_\infty = \alpha N^-$. The recombination rate α in (29) is

$$\alpha(t) = \alpha_3(R_E)n^-(R_E,t)/N^- = N\int_0^{R_E} 4\pi R^2 \sum_{i=-E}^{C}\left[n_i(R,E_i,t)\sum_{f=-V}^{-E} k_{if}(R) - \sum_{f=-M}^{-E} n_f(R,E_f,t)k_{fi}(R)\right], \tag{30}$$

which can be determined from the appropriate solutions of the Boltzmann equation (21) for the phase densities n_i and from knowledge of the energy-change collisional rates $k_{if}(R)$. When the ion density $N^\pm$ is increased, the ion–ion interaction V that appears in (21) and in k_{if} can no longer be assumed to be Coulombic but is the solution of Poisson's equation

$$\nabla^2 V = \frac{4\pi e^2}{\varepsilon}\left[N^+ \exp(V/kT) - n^-(R,t)\right] \tag{31}$$

in the reference frame of the positive ion. The dielectric constant of the background gas is ε. Thus the full basic theory of (30) involves the self-consistent solutions of (21) and (31) inserted in (30) for α.

Two theoretical methods—the "separable-equations" method and the "distribution-in-length-between-collisions" method—have been proposed (Flannery, 1982a) for the solution of (21) for the phase-space densities n_i such that α is obtained from (30) as a general function of gas density N.

Under quasistationary conditions $(\partial/\partial t)\int_0^{R_E} n^- \, d\mathbf{R} \ll \alpha N^-$, valid when few ions are present within the recombination sphere, and $(\partial/\partial t)\int_{R_E}^{R} n^- \, d\mathbf{R}$ is negligible since transport only is in effect for $R \geqslant R_E$ to give

$$4\pi R^2 J_i(R,t) = \alpha_3(R) n^-(R,t) = \alpha N^-, \qquad R \geqslant R_E, \tag{32}$$

a constant flux. Equation (27) may be solved for $n^-(R \geqslant R_E)$ in terms of α which, when replaced by $\alpha_3 n^-/N$, yields

$$n^-(R) = \frac{4\pi D\tilde{R}}{\{\alpha_3(R)\exp(-V(R)/kT) + 4\pi D\tilde{R}\}} N^- \exp(-V/kT), \qquad R \geqslant R_E, \tag{33a}$$

where

$$\tilde{R} = \left[\int_R^\infty \exp(-V/kT) R^{-2}\, dR\right]^{-1}, \qquad kT \equiv De/K \tag{33b}$$

is R in the absence of interaction, and reduces to $R_e[1 - \exp(-R_e/R)]^{-1}$ for a pure Coulomb attraction whose natural unit R_e is (e^2/kT) where V and kT are equal.

The steady state recombination rate is therefore

$$\alpha = \alpha_3(R_E) n^-(R_E)/N^- = \alpha_{TR}\alpha_{RN}/(\alpha_{TR} + \alpha_{RN}), \tag{34}$$

where the rate of *transport* of ions to R_E is

$$\alpha_{TR} = 4\pi D \Big/ \int_{R_E}^\infty \exp(KV/De) R^{-2}\, dR \equiv 4\pi D\tilde{R}_E \tag{35}$$

and where the rate of *reaction* of ions within R_E is

$$\alpha_{RN} = \alpha_3(R_E)\exp(-V(R_E)/kT). \tag{36}$$

The reaction rate α_{RN} from (30) is the recombination rate α for the case when a Boltzmann distribution $N^- \exp(-V/kT)$ of ions are maintained, which occurs in (33a) when $\alpha_{TR} \gg \alpha_{RN}$ as at low gas density N. At high N, $\alpha_{TR} \ll \alpha_{RN}$, $n(R_E) \to 0$ so that $\alpha \to \alpha_{TR}$. Thus, the recombination rate is determined by the rate-limiting step of reaction versus transport at both low and high N. This basic theory, therefore, not only reproduces the correct limits at low and high N but also yields (Flannery, 1982a) an initial nonlinear N variation consistent with Thomson (1924) and with Bates and Mendaš (1978a). For intermediate N, transport and reaction are coupled as in (34).

Since α_3 and hence α_{RN} is internally dependent on the phase densities $n_i(R, E_i, t)$ via (28) and (22), we note with this required knowledge of n_i that α may, of course, be determined directly from (30) rather than from (34). Not only does (34), however, promote further physical and basic under-

standing of recombination, it is also very effective when alternative means are used to deduce $\alpha_{RN}(R_E)$ as, for example, in Sections II.B and IV. With predetermined knowledge of $\alpha_3(R)$, then (23) with (25b) and (28) may be written as

$$-\frac{\partial n^-}{\partial t}(\mathbf{R},t)+\nabla\cdot J_i(\mathbf{R},t)=\alpha_3(R)n^-(\mathbf{R},t)\delta(\mathbf{R}-\mathbf{R}_E), \tag{37}$$

which uniquely identifies α_3 as the strength (in cm^3/s) of a sink within $\mathbf{R}_E$.

The density (33a) with (34)–(36) can be expressed as

$$n^-(R)=\left[1-\frac{\alpha}{\alpha_{TR}}(\tilde{R}_E/\tilde{R})\right]N^-\exp(-V/kT)\equiv\mathscr{P}^e(R,R_E)N^-\exp(-V/kT), \tag{38}$$

where $\mathscr{P}^e$, which represents the fractional departure of n^- from Boltzmann equilibrium, can be shown (Flannery 1982a) to be the probability of expansion of an isolated R ion pair in the presence of a sink at R_E. The corresponding probability of contraction is

$$\mathscr{P}^c(R,R_E)=1-\mathscr{P}^e=\frac{\alpha}{\alpha_{TR}}(\tilde{R}_E/\tilde{R}) \tag{39}$$

and hence

$$\alpha=\mathscr{P}^c(R_E,R_E)\alpha_{TR}=\mathscr{P}\alpha_{TR} \tag{40a}$$

$$=\mathscr{P}^e(R_E,R_E)\alpha_{RN}, \tag{40b}$$

which identifies $\mathscr{P}$, the probability of recombination $\alpha_{RN}/(\alpha_{TR}+\alpha_{RN})$ of ion pairs transported to R_E at rate α_{TR}, with the probability $\mathscr{P}^c$ of further contraction of an R_E ion pair. The transient escape probability may, therefore, be determined directly from

$$-\frac{\partial\mathscr{P}^c}{\partial t}(R,t)+\exp(V/kT)\,\nabla\cdot[D\exp(-V/kT)\nabla\mathscr{P}^c(R,t)]=\alpha_3(R)\mathscr{P}^e(\mathbf{R},t)\delta(\mathbf{R}-\mathbf{R}_E) \tag{41}$$

subject to $\mathscr{P}^e(R\to\infty,t)\to 1$. The termolecular rate is given then by (40b).

B. Time-Dependent Solutions

The transient recombination rates can be obtained directly from (30) with the solution of the Boltzmann equation (21) for the transient phase densities. Provided α_3 is predetermined, important basic and physical insight

can, however, be extracted (Flannery, 1981c,d, 1982a,b) from the continuity equation (37), which for a spherical interaction $V(R)$ becomes

$$-\frac{\partial n^-}{\partial t}(R,t)+\frac{1}{R^2}\frac{\partial}{\partial R}(R^2 J_i)=\alpha_3(R)n^-(R,t)\delta(R-S)/4\pi R^2, \quad (42a)$$

where S is now identified with the radial extent of the sink and where the inward current (/cm^2 s) is

$$J_i(R)=D\exp(-V/kT)(\partial/\partial R)[n^-(R)\exp(V/kT)]. \quad (42b)$$

When a dissociated pair A and B is generated instantaneously within a gas or liquid medium then the (A–B) pair may react internally or escape by diffusional drift in the presence of a sink to infinite separation. The key quanity in this *geminate recombination* process is the probability $\mathscr{P}(t)$ or $\sum(t)$ for recombination or survival, respectively, of the dissociating pair at time t. When reaction occurs between a central species A and another of the species B created within the medium by a continuous source at infinity (or else by escape from geminate recombination), this recombination is *homogeneous* and is characterized by an effective two-body rate coefficient $\alpha(t)$ cm^3/s appropriate to termolecular reactions.

The boundary conditions appropriate to homogeneous recombination are

$$\left.\begin{matrix} n^-(R,t=0) \\ n^-(R\to\infty,t) \end{matrix}\right\} = N^- \exp(-V/kT), \quad (43)$$

which correspond to a Boltzmann distribution of ions being initially produced over all space and being continuously generated at infinite distance from the positive ions. The boundary conditions appropriate to geminate recombination are

$$\begin{aligned} n^-(R,t=0) &= \mathscr{N}\exp(-V/kT)\delta(R-R_0)/4\pi R_0^2, \\ n^-(R\to\infty,t) &= 0 \end{aligned} \quad (44)$$

for an instantaneous production of $\mathscr{N}\exp(-V(R_0)/kT)$ ions by a spherical surface source at distance R_0 from the central positive ion, i.e., R_0 ion pairs are initially generated.

A third boundary condition at S to solution of the equation homogeneous to (42a) is already incorporated within (42a) and is extracted by integration over the volume of the S sphere to give the quasistationary condition

$$4\pi S^2 J_i(S,t)=\alpha_3(S)n^-(S,t) \quad (45a)$$

provided $\frac{4}{3}\pi S^3 N^{\pm} \ll 1$ such that few ions are present in the "recombination" sphere. Thus, (45a) equates the frequency of ions transported to S with the frequency $\alpha_3 n^-$ of absorption. With (41) or (42) transformed to the

$\tilde{R}$ variable (33), then (45a) is

$$\tilde{S}(\partial/\partial\tilde{R})[n^- \exp(V/kT)]_S = (\alpha_{RN}/\alpha_{TR})_S[n^-(S,t)\exp V(S)/kT] \quad (45b)$$

or

$$\tilde{S}(\partial/\partial\tilde{R})\mathscr{P}^e(\tilde{R},\tilde{S}) = (\alpha_{RN}/\alpha_{TR})_S\mathscr{P}^e(\tilde{R},\tilde{S}), \qquad \tilde{R} = \tilde{S} \quad (45c)$$

i.e., when the reaction rate $\alpha_{RN} \gg \alpha_{TR}$ as at high gas densities N, then $n(S,t) \to 0$ for spontaneous reaction, and when $\alpha_{RN} \ll \alpha_{TR}$ for weak reaction as low N, then $J_i(S,t)$ vanishes to give a Boltzmann distribution. Thus (45) is, in general, a radiation boundary condition since not all ions approaching S are absorbed and is analogous to that met in problems on heat conduction.

Homogeneous recombination: The exact solution of (40) for homogeneous recombination (42) under zero field ($V = 0$) when $\tilde{R} = R$ is (Flannery, 1982a)

$$n_d^-(R,t) = N^-\left[1 + \left(\frac{\alpha}{\alpha_d}\right)\left(\frac{S}{R}\right)\{\exp(2\Omega\chi)\exp\chi^2\,\mathrm{erfc}(\chi+\Omega) - \mathrm{erfc}\,\Omega\}\right], \quad (46)$$

where the error function (or probability integral) is

$$\mathrm{erfc}\,\chi = \frac{2}{\sqrt{\pi}}\int_\chi^\infty \exp(-\chi^2)\,dx. \quad (47)$$

The time dependence of (46) appears in both

$$\chi(t) = [1 + (\alpha_3/\alpha_d)](Dt/S^2)^{1/2} \equiv (\alpha_3/\alpha)(Dt/S^2)^{1/2}, \quad (48a)$$

where α_3 and α_d denote the reaction and diffusion-transport rates (36) and (35), respectively, in the absence of drift ($V = 0$) such that α is $\alpha_3\alpha_d/(\alpha_3 + \alpha_d)$, and in

$$\Omega(t) = (R - S)/2(Dt)^{1/2}, \quad (48b)$$

which vanishes at the sink. The exact transient recombination rate is therefore

$$\begin{aligned}\alpha(t) &= 4\pi S^2 D(dn_d^-/dR)_S/N^- = \alpha_3 n_d^-(S,t)/N^- \\ &= \alpha[1 + (\alpha_3/\alpha_d)\exp\chi^2\,\mathrm{erfc}\,\chi].\end{aligned} \quad (49a)$$

At high gas density N, $\alpha_3 \gg \alpha_d \simeq \alpha$, such that $n_d^-(S,t)$ vanishes and $\chi \to \infty$ to give

$$n_d^{(s)}(R,t) = N^-\left[1 - \left(\frac{S}{R}\right)\mathrm{erfc}\,\frac{(R-S)}{2(Dt)^{1/2}}\right]. \quad (50a)$$

From (49a), or directly from

$$\alpha(t) = \frac{d}{dt}\int_S^\infty 4\pi R^2[n_d^-(R,t) - N^-]\,dR/N^-, \quad (50b)$$

since $n^-(R \leqslant S)$ vanishes, the recombination rate is

$$\alpha_d^{(s)}(t) = \alpha_d[1 + S/(\pi Dt)^{1/2}] \tag{50c}$$

appropriate to diffusion (d) controlled transport and spontaneous (s) reaction for an initial random distribution N^-. As $t \to 0$, $n_d \to N^-$ and $\alpha \to$ the assumed infinite rate of reaction. As $t \to \infty$, $n_d \to N^-[1 - S/R]$ and $\alpha \to \alpha_d$, the steady state density and rate, respectively.

Although exact solutions of (40) have not yet been obtained for general $V(R)$, Flannery (1982a,b, 1981c,d) has shown how closed-form, highly accurate analytical solutions of (40) may be determined by transformation to variable $\tilde{R}$ of (33). For homogeneous recombination (42) then (Flannery, 1982a,b)

$$n^-(R,t) = N^- \exp(-V/kT)\left[1 + \left(\frac{\alpha}{\alpha_{TR}}\right)\left(\frac{\tilde{S}}{\tilde{R}}\right) \times \{\exp(2\Omega\tilde{\chi})\exp\tilde{\chi}^2 \operatorname{erfc}(\tilde{\chi} + \Omega) - \operatorname{erfc}\Omega\}\right] \tag{51}$$

with

$$\tilde{\chi}(t) = \left(\frac{\alpha_{RN}}{\alpha}\right)\left(\frac{Dt}{S^2}\right)^{1/2} \exp(V(S)/kT)\left[S\int_S^\infty \exp(V/kT)R^{-2}\,dR\right]^{-1}, \tag{52}$$

where α, α_{TR}, and α_{RN} are given by (34)–(36). The transient recombination rate

$$\alpha(t) = \alpha_3 n^-(S,t)/N^- = \alpha[1 + (\alpha_{RN}/\alpha_{TR})\exp\tilde{\chi}^2 \operatorname{erfc}\tilde{\chi}]. \tag{53}$$

Since

$$\exp\chi^2 \operatorname{erfc}\chi \to \begin{cases} 1 - \left(\dfrac{2}{\pi^{1/2}}\right)\chi + \chi^2 - \left(\dfrac{4}{3\pi^{1/2}}\right)\chi^3 \cdots, & t \to 0 \\ \left(\dfrac{1}{\chi\pi^{1/2}}\right)(1 - \frac{1}{2}\chi^2 + \frac{3}{4}\chi^4 \cdots), & t \to \infty \end{cases} \tag{54}$$

then

$$\alpha(t \to 0) = \alpha_{RN}\left[1 - \frac{2}{\pi^{1/2}}\frac{\alpha_{RN}}{\alpha_{TR}}\left(\frac{Dt}{S^2}\right)^{1/2}\frac{\tilde{S}}{S}\exp V(S)/kT\right] \tag{55}$$

decreases initially from the reaction rate to the long-time rate

$$\alpha(t \to \infty) = \alpha\left[1 + \left(\frac{\alpha}{\alpha_{TR}}\right)\frac{S}{\tilde{S}}\left(\frac{S^2}{\pi Dt}\right)^{1/2}\exp - V(S)/kT\right], \tag{56}$$

which tends to α, the steady state rate (34). Not only will the variation of α with N show the transition via (34) from reaction-controlled recombination to transport-controlled recombination as N increases, but the variation of (53) for $\alpha(t)$ with t for fixed N will exhibit interesting features basic to the physics of recombination. The time variation of the above transient rates are amplified best at high gas densities when $\alpha_{RN} \gg \alpha_{TR} \approx \alpha$. For a pure Coulomb attraction between the ions,

$$\tilde{\chi} = \left(\frac{\alpha_{RN}}{\alpha}\right)\tau^{1/2}\left(\frac{R_e}{S}\right)[\exp(R_e/S) - 1]^{-1}, \tag{57}$$

where τ is time in units of (S^2/D), the time approximately required for an ion to diffuse from the boundary to the center of the sink.

Figure 1 illustrates the variation of $\alpha(t)$ with t for several values (1, 2, 3, 5, and 10) of the gas density N (in units of N_L, 2.69×10^{19} cm^{-3}, the number density at STP). These rates (Flannery, 1981d, 1982a) are appropriate to a fictitious (but representative) case of equal masses ($M = 16$ amu) of the

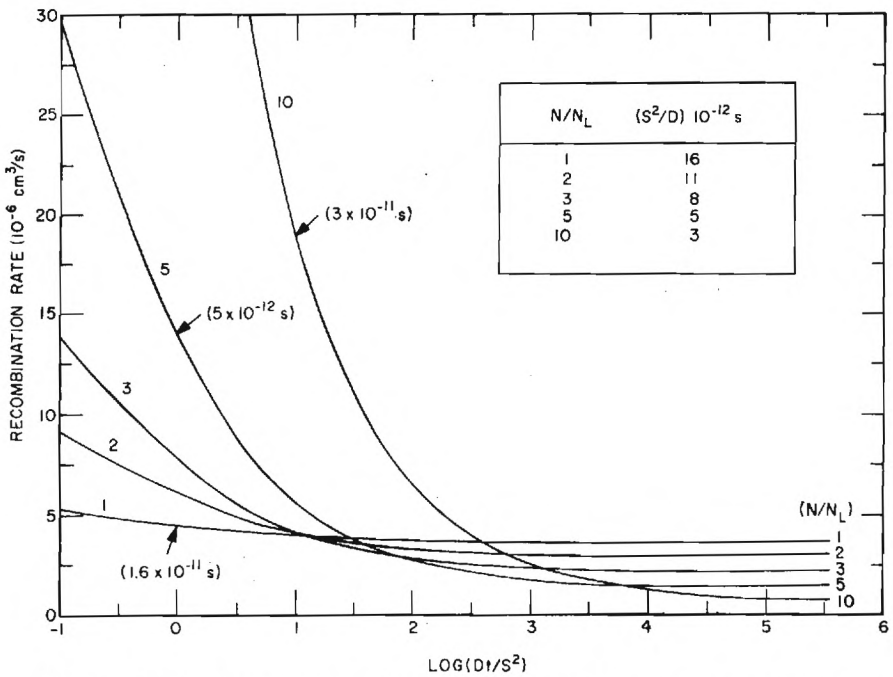

Fig. 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities, as indicated in units of Loschmidt's number N_L ($2.69\ 10^{19}$ cm^{-3} at STP). Characteristic times (S^2/D) for diffusion are also indicated.

ionic species with mobility 2 $cm^2/V\,s$ in an equal-mass gas and with δ_i in Eq. (12) taken to be 0.6.

Since the initial ion distribution is assumed Boltzmann equilibrium, the initial rate of recombination $\alpha(t = 0)$ is simply the reaction rate α_{RN}, in accord with (55). The ions then begin their transport and replace the reacted ions within a time $\sim(S^2/D)$ s. Since the recombination is determined by the rate-limiting step of reaction and transport, its variation with time is best observed at high gas densities N where $\alpha_{RN} \gg \alpha_{TR}$ such that α decreases from α_{RN} to α_{TR}, the steady state limit at $t \gg (S^2/D)$. Variation of α with t for the case $N \sim 10N_L$, for example, reflects the change in α from reaction controlled to transport controlled. The reaction rate at high $N \gtrsim 5N_L$ is so large because the radial extent S of the sink becomes so contracted that the enhancement of ions at its boundary is locally very large and offsets the inherent reduction in cross section. For $N \sim N_L$ and lower, the transport is always faster than the reaction such that the reaction rate limits the rate of recombination at all times, and a near straight-line dependence is observed as in Fig. 1. The steady state limit is, of course, independent of any initial condition adopted. Figure 1 is therefore a striking illustration of the transition in recombination from initial reaction above to the limiting step of reaction/transport.

At high N, the recombination steady state rate tends to the rate of transport to S which is

$$\alpha_D = 4\pi DS, \tag{58a}$$

$$\alpha_K = 4\pi S^2 K|-\nabla V|_S/e = 4\pi DS^2[-\nabla(KV/De)]_S, \tag{58b}$$

and

$$\alpha_{TR} = 4\pi D\left[\int_S^\infty \exp(KV/De)R^{-2}\,dR\right]^{-1} \equiv 4\pi D\tilde{S}, \tag{58c}$$

for pure diffusion, pure drift, and combined diffusional drift, respectively. For a long-range attraction $V/kT \sim -(R_n/R)^n$ where R_n is the natural unit peculiar to V then the drift rate

$$\alpha_K = 4\pi nKe(R_n/R_1)(R_n/R)^{n-1} \tag{58d}$$

diverges for $n > 1$ in the limit of small $R \ll R_n$, in contrast to the full diffusional-drift rate, written in terms of the incomplete and full gamma functions γ and Γ, respectively, as

$$\alpha_{TR} = 4\pi nDR_n/\gamma\left(\frac{1}{n}, \left(\frac{R_n}{R}\right)^n\right) \xrightarrow{R \ll R_n} 4\pi nDR_n/\Gamma\left(\frac{1}{n}\right), \tag{58e}$$

which tends to a constant limit at small R. Only for pure Coulomb attraction ($n = 1$) do the drift and diffusional drift results agree in the small R limit, thereby showing that Langevin's method based on drift is fortuitous in the sense that it yields the correct limit only for Coulombic attraction. It is also interesting to note that V is fully acknowledged by simply replacing S in the field-free case (58a) by $\tilde{S}$ in (58c); and that (58a) alone is incorrect if realistic $S \sim (R_e\lambda)^{1/2} \sim N^{-1/2}$ are adopted, rather than arbitrarily choosing S to be R_e, which enforces agreement between α_D and α_K. These notes help resolve previous confusion that existed (see Flannery, 1976, p. 423) between treatments based either on pure diffusion (Harper, 1932) or on pure drift (Langevin, 1903). Neither treatment is rigorously correct, and both diffusion and drift must be coupled, although any error in Langevin's result α_K in (58b) for a pure Coulomb attraction only disappears in the high-N limit when $S \ll R_e$ unlike that involved with (58a). The diffusional-drift coupling that ensures Boltzmann equilibrium is very important to the general solution of the Boltzmann equation (21) for the phase densities (Flannery, 1982a) at intermediate and high N.

For recombination in a gas (58a) and (58c) are the results of Harper (1932) and of Bates (1975). For coagulation of colloid suspensions in a liquid of permittivity ε, similar expressions (with $R_e = Z_1 Z_2 e^2/\varepsilon kT$) have been obtained by Smoluchowski (1917) and by Debye (1942). For this reason the diffusional-drift equation of continuity (42) is sometimes referenced as the Debye–Smoluchowski equation derived originally from a stochastic random-walk picture of the process but modified here to automatically include the radiation boundary condition (45). The interesting feature is that it is a natural consequence of the basic microscopic treatment (Flannery, 1982a) outlined in Section III.A that therefore provides its full generalization via (28) to an arbitrary sink based on detailed collisional kinetics which in turn depends on the phase-space densities $n_i(R, E_i, t)$. However, with this knowledge of n_i, the steady state α can be obtained directly from (30), rather than from the solution of (42) with (28).

Geminate recombination: Time dependences as (53) are valuable not only in the analysis of laboratory experiments and in medical radiology, but also in situations where intense ionization is deposited into or produced within a localized system either by a high energy beam of particles or radiation such that many ions may diffuse out of the localized system before neutralization occurs and cause significant damage. The rate of disappearance of the ion pairs scattered along the track of the ionizing particles or rays is time dependent and represents a key problem. For geminate recombination (44), the highly accurate analytical time-dependent solution for general

$V(R)$ is (Flannery, 1982a,b)

$$n^{-}(R,t;R_0,S)=\frac{\mathscr{N}\exp(-V/kT)}{(4\pi R_0^2)}\left(\frac{\tilde{R}_0}{\tilde{R}}\right)\frac{1}{(4Dt)^{1/2}}\left[\frac{1}{\sqrt{\pi}}\exp(-\Omega_0^2)+\exp(-\Omega_1^2)\right.$$
$$\left.-2\tilde{\chi}\exp(\tilde{\chi}^2)\exp(2\Omega_1\tilde{\chi})\operatorname{erfc}(\tilde{\chi}+\Omega_1)\right] \tag{59a}$$

in terms of $\tilde{R}$ of (33b), of (52) or (57) for $\tilde{\chi}$, and of the time-dependent dimensionless quantities

$$\Omega_0(R,t)=\frac{(R-R_0)}{(4Dt)^{1/2}},\qquad \Omega_1(R,t)=\frac{(R+R_0-2S)}{(4Dt)^{1/2}}. \tag{59b}$$

The survival probability that each pair has not reacted in geminate recombination,

$$\sum(t)=\frac{1}{\mathscr{N}_0}\int_{\mathscr{V}} n^{-}(R,t;R_0,S)\,d\mathbf{R}, \tag{60a}$$

where the integration is over all volume $\mathscr{V}$ external to the surface $\mathscr{S}$ of the spherical sink is best evaluated indirectly from

$$\sum(t)=1-\mathscr{P}(t)=-\frac{1}{\mathscr{N}_0}\int_0^t v(t)\,dt, \tag{60b}$$

where $\mathscr{N}_0$ is the number $\mathscr{N}\exp(-V(R_0)/kT)$ initially generated. Since J in $(R\to\infty)$ of (42) vanishes, the frequency of recombination is

$$v(t)=-\int_{\mathscr{S}}(\partial n^{-}/\partial t)\,d\mathbf{R}=\alpha_3(S)n^{-}(S,t;R_0,S). \tag{61a}$$

Without loss of generality, a coincident source and sink $[R_0=S,\ \Omega_{0,1}(S,t)=0]$ can be assumed so that

$$v(t)=-\frac{\mathscr{N}\exp(-V(R_0)/kT)}{4\pi S^2}\frac{\alpha_3}{(4Dt)^{1/2}}\frac{d}{d\tilde{\chi}}\left[\exp\tilde{\chi}^2\operatorname{erfc}\tilde{\chi}\right] \tag{61b}$$

in (60b) to give the probability of recombination

$$\mathscr{P}(t)=\left(\frac{\alpha}{\alpha_{\mathrm{TR}}}\right)\left[1-\exp\tilde{\chi}^2(t)\operatorname{erfc}\tilde{\chi}(t)\right], \tag{62}$$

which initially increases from zero as $\sim(\alpha_{\mathrm{RN}}/\alpha_{\mathrm{TR}})t^{1/2}$ to a saturation value of $(\alpha/\alpha_{\mathrm{TR}})$. From (62), (53), and (34) the following exact relations

$$\alpha(t)=\alpha_{\mathrm{RN}}\sum(t)=\alpha_{\mathrm{RN}}[1-\mathscr{P}(t)]\xrightarrow{t\to\infty}\alpha_{\mathrm{TR}}\mathscr{P}(\infty)=\alpha_{\mathrm{RN}}\sum(\infty) \tag{63}$$

between the transient rate $\alpha(t)$ for homogeneous recombination and the transient recombination and escape probabilities $\mathscr{P}(t)$ and $\sum(t)$, respectively, for geminate recombination are immediately established [cf. (40)]. Thus, the same key quantities appear in two distinct time-dependent problems: homogeneous recombination, where the process is driven by a source operating continuously at infinity; and intrapair (geminate) recombination, where the process is initially established by an instantaneous source of ion pairs within the medium (as produced by a laser burst) and is controlled by the relative reaction and transport rates. The processes are similar in that both can be described by the same diffusional-drift (Debye–Smoluchowski) equation (42) solved to different boundary conditions (43) or (44).

C. *Function of Ion Density*

All previous theoretical and experimental studies of ion–ion recombination pertain to a dilute degree of ionization with ion densities $N^{\pm} \sim 10^8\ \text{cm}^{-3}$. Ion–ion recombination plays a key role (Flannery, 1979) in populating the upper electronic levels of rare-gas halide lasers, which operate not only at high gas pressure ($\sim\frac{1}{2} - 10$ atm) but also at relatively high ion densities $N^{\pm} \sim 10^{12} - 10^{14}\ \text{cm}^{-3}$. As $N^{\pm}$ is raised, the interaction between the positive and negative ions is no longer pure Coulombic but depends on the screening due to the other ions via their net charge density distribution which, in turn, is coupled to the recombination sink via α, which contains an explicit dependence on V. Repulsion between like ions and competition between the sinks for the flux may also become important.

On integration of (42a), which explicitly neglects competition between sinks [see Eq. (75)] over a volume of an S sphere and on setting $\partial n/\partial t \sim \alpha N^+ N^-$, we note that the radiation boundary condition (45a) implies that $\frac{4}{3}\pi S^3 N^{\pm} \ll 1$. Few sinks must therefore be present in the "recombination" sphere of radius $S \sim 550$ Å at STP and so $N^{\pm} \ll 2 \times 10^{15}\ \text{cm}^{-3}$, which is also consistent with the neglect of ion–ion collisions in the original Boltzmann equation (21).

The interaction energy V between the ions is now determined from appropriate solutions of Poisson's equation

$$\nabla^2 V = (4\pi e/\varepsilon)\rho(R), \tag{64}$$

where ρ is the charge density distribution $[n^+(R) - n^-(R)]e$ in terms of the positive and negative ion densities $n^{\pm}(R)$ and where ε is the dielectric constant of the gas Z. At density N of a gas of polarizability p, ε is $(1 + 4\pi Np)$ which, for Xe, is $(1 + 1.4\ 10^{-3} N/N_L)$, in effect unity for $N < 25$ times N_L, the number density ($2.69 \times 10^{19}\ \text{cm}^{-3}$) at STP. The net inward steady state

flux (s^{-1}) of positive ions toward a positive ion is

$$F_{IN}^{++}(R) = -4\pi R^2\left[-D^+\frac{dn^+(R)}{dR} + n^+(R)\left(\frac{K^+}{e}\right)\frac{\partial V}{\partial R}\right], \tag{65}$$

where D^+ and K^+ are $2D_1$ and $2K_1$, respectively, in terms of the diffusion coefficient D_1 and mobility K_1 for positive ions 1. The net inward flux of negative ions 2 toward a positive ion 1 is, as before,

$$F_{IN}^{-+}(R) = 4\pi R^2\left[D\frac{dn^-(R)}{dR} + n^-(R)\left(\frac{K}{e}\right)\frac{\partial V}{\partial R}\right], \tag{66}$$

where D and K and the respective sums $(D_1 + D_2)$ and $(K_1 + K_2)$ of the diffusion coefficients D_i and mobilities K_i for ion i ($\equiv 1, 2$). In the reference frame of the positive ions, $F_{IN}^{+\,+}$ vanishes and integration of (65) yields

$$n^+(R) = N^+\exp[V(R)/kT], \tag{67}$$

where T is given by De/Kk under conditions when the Einstein relation no longer holds. Hence Poisson's equation for a R-symmetric distribution is

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial V}{\partial R}\right) = \frac{4\pi e^2}{\varepsilon}\left[N^+\exp(V(R)/kT) - n^-(R)\right], \tag{68}$$

where the negative ion density $n^-(R)$ is obtained from the equation of continuity (27) of quasistationary flux at R, i.e., from

$$4\pi R^2\left[D\frac{dn^-(R)}{dR} + n^-(R)\frac{K}{e}\frac{\partial V}{\partial R}\right] = \alpha_3(R)n^-(R). \tag{69}$$

The solution of (68) for V is coupled to the solution of (69) for $n^-(R)$, which in turn is coupled via $\alpha_3(R)$ in (28) to the solution of coupled integro-differential equations (21) for the phase-space distributions $n_i(R, E_i)$ of negative ions. Application of the preceding theory represents a formidable yet feasible task. With the aid of (38), the self-consistent interaction $V(R)$ as a function of N and R is given by the appropriate solution of

$$\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial(V/kT)}{\partial R} = -\left(\frac{1}{2R_S^2}\right)\left[\exp(V/kT) - \left\{1 - \left(\frac{\alpha}{\alpha_{TR}}\right)\frac{\tilde{R}_E}{\tilde{R}}\right\}\exp(-V/kT)\right], \quad R \geqslant R_E, \tag{70}$$

where the "screening" distance is

$$R_S = (8\pi N^{\pm}R_e/\varepsilon)^{-(1/2)}, \tag{71}$$

in terms of $R_e = e^2/kT$. The $\{\ \}$ term, which depends on V, N, and R in (70), tends to unity at low N for all R and increases at high N, from zero at $R \approx R_E$ to unity as $R \to \infty$. As $R_S \to \infty$, the interaction (V/kT) from (70) is pure Coulomb.

When $V \ll kT$, (70) may be solved exactly (Flannery, 1981c, 1982a) to give

$$V(R) = -[\tfrac{1}{2}(\alpha/\alpha_K) + (1 - \tfrac{1}{2}(\alpha/\alpha_K))\exp(-R/R_S)](e^2/R) \tag{72}$$

such that at low N when $\alpha \ll \alpha_K$, the Langevin rate $4\pi Ke$,

$$V(R) \to -(e^2/R)\exp(R/R_S), \tag{73}$$

the Debye–Hückel interaction (DH) while at large N, then

$$V(R) \to -(e^2/2R)[1 + \exp(-R/R_S)] \tag{74}$$

the mean of the pure Coulomb and DH interactions which is consistent with the choice $\alpha \sim \alpha_K$.

Direct numerical solution of (70) subject to (72) as boundary condition at asymptotic R when $V \ll kT$ shows that (72) remains a highly accurate solution for all R. At low N, the criterion $V \ll kT$ is satisfied in the important region $R \approx R_E$ when $R_S \gg R_e$, which implies via (71) that many ions are present within the R_S sphere and $N^{\pm} \ll 2 \times 10^{14}\ \text{cm}^{-3}$. As N increases, the radius R_E of the reaction zone decreases as $(R_e/N)^{1/2}$, which at high N becomes $\ll R_e$ such that (74) is then pure Coulomb at R_E.

As $N^{\pm}$ is increased, the ion pairs and distributed over all space. Coupling between geminate and homogeneous recombination may become important and can be acknowledged by the following equation:

$$\frac{\partial \rho(R,t)}{\partial t} = \nabla \cdot \hat{\mathscr{J}}_i \rho - \alpha_3 \rho \delta(\mathbf{R} - \mathbf{S}) - \alpha(t)\langle \rho(t)\rangle_s \rho(R,t), \qquad R \geqslant S \tag{75}$$

for the cm^{-6} concentration ρ of R ion pairs such that $\rho\, d\mathbf{R}$ is the concentration of ion pairs with internal separation $\mathbf{R}$ in the interval $d\mathbf{R}$ about $\mathbf{R}$. In (75) the density of unreacted ion pairs (with $R > S$) is

$$\langle \rho(t)\rangle_s = \int \rho(R,t)\, d\mathbf{R} = \int_S^{\infty} 4\pi R^2 \rho(R,t)\, dR \tag{76}$$

and $\hat{\mathscr{J}}_i\, n$ is simply the net inward diffusional drift current J_i in (42b) and the end two terms of (75) represent geminate and homogeneous recombination, respectively. Substitute

$$\rho(R,t) = C(t)g(R,t) \tag{77}$$

in (75) where C satisfies

$$\frac{\partial C(t)}{\partial t} = -\alpha\langle g(t)\rangle_s C^2(t) \tag{78}$$

such that the probability density or pair correlation function $g(R, t)$ satisfies the usual Debye–Smoluchowski equation

$$\frac{\partial g}{\partial t} = \nabla \cdot \hat{\mathscr{J}}_i g - \alpha_3 g \delta(\mathbf{R} - \mathbf{S}) \tag{79}$$

for an isolated sink. Hence

$$C(t) = C_0 \Big/ \left[1 + C_0 \int_0^t \alpha(t) \langle g(t) \rangle_s \, dt \right], \tag{80}$$

where C_0 is the initial concentration of ion pairs, describes the time decay of all ion pairs via recombination and $g(R, t)$ describes the spatial distribution R ion pairs. The recombination rate

$$\alpha(t) = -\frac{d}{dt} \left[\int_s^\infty 4\pi R^2 \rho(R, t) \, dR \right] \Big/ N^+ N^- + F_\infty / N^+ \tag{81}$$

therefore satisfies

$$\alpha(t)[1 - \langle g(t) \rangle_s^2 C^2(t)/N^+ N^-] = \alpha_0(t) C(t)/N^+, \tag{82}$$

where α_0 is the rate that is obtained from appropriate solution of (76) for an isolated sink (or constant C) provided few ions are present within the recombination volume, as for quasistationary conditions when $N^\pm \ll 10^{15}$ cm^{-3}. When the initial concentration C_0 and the time t_0 for geminate recombination are sufficiently small such that

$$C_0 \int_0^t \alpha(t) \langle g(t) \rangle_s \, dt \ll 1, \tag{83}$$

then (80) and (82) reduce to the case of an isolated sink with associated rate α_0.

IV. Recombination Rates for Various Rare-Gas Halide Systems

Figures 2 and 3 show displayed rates α, determined from Section II.B, as a function of gas density N for the processes

$$\begin{aligned} &Kr^+ + F^- + M \longrightarrow KrF^*(B, C, D) + M \; (M \equiv Ne, Ar, Kr, Xe), \\ &Kr_2^+ + F^- + M \longrightarrow KrF^*(B, C, D) + Kr + M, \end{aligned} \tag{84}$$

which involve atomic and molecular positive ions and

$$\begin{aligned} &Xe^+ + Cl^- + M \longrightarrow XeCl^*(B, C, D) + M, \\ &Xe_2^+ + Cl^- + M \longrightarrow XeCl^*(B, C, D) + Xe + M \end{aligned} \tag{85}$$

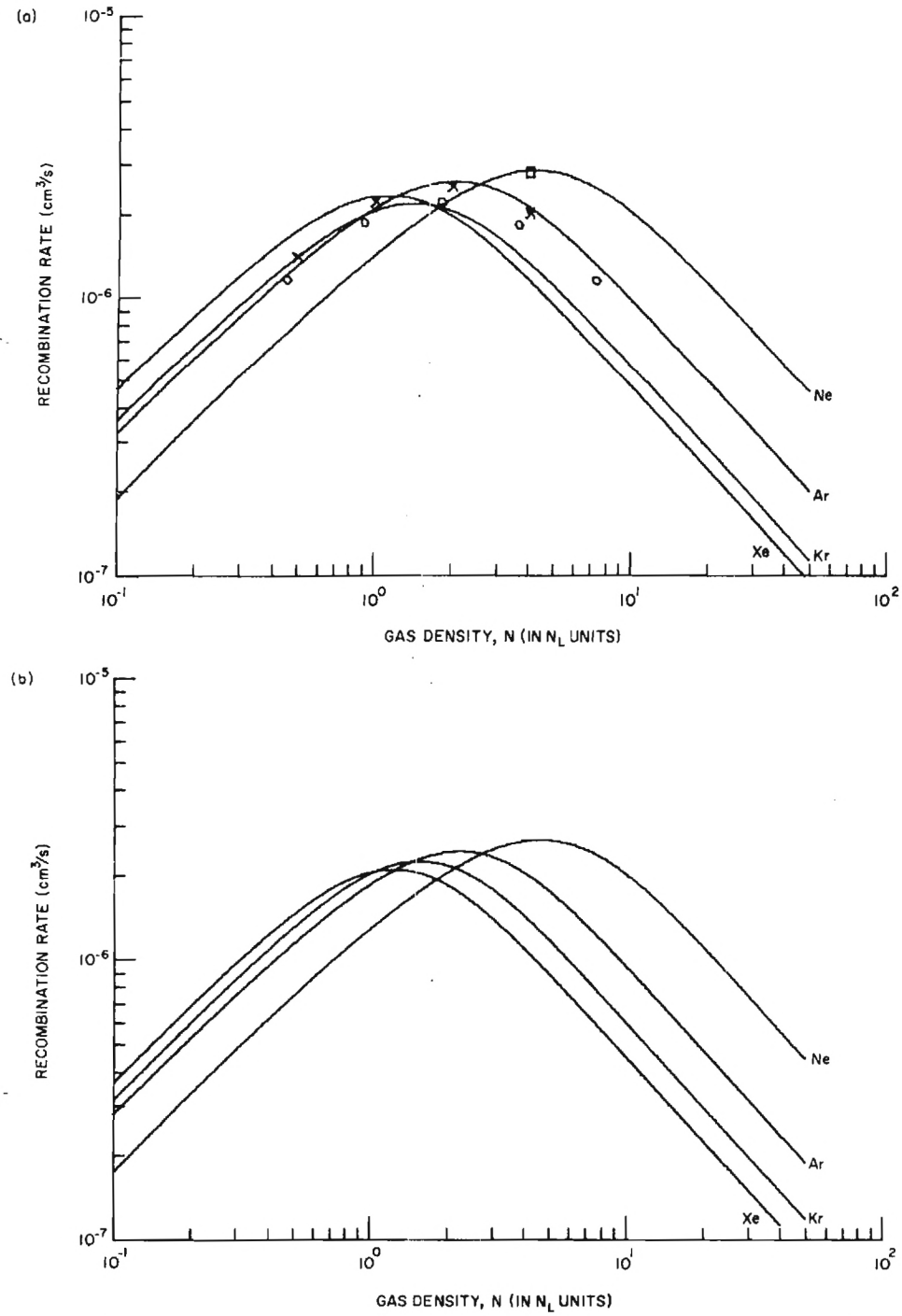

Fig. 2. Recombination rate coefficient $\alpha(\mathrm{cm}^3/\mathrm{s})$ at 300 K for (a) Kr^+-F^- and (b) $Kr_2^+-F^-$ in various rare gases Ne, Ar, Kr, and Xe of density N (in units of Loschmidt's number density $N_L = 2.69\ 10^{19}$ at STP). ——: present treatment, Sections II.B and III.C. □, ×: Universal Monte Carlo (hard-sphere) plot (Bates, 1980c) for Ne and Ar, respectively. ○: Monte Carlo (polarization) results (Morgan *et al.*, 1981) for Ar.

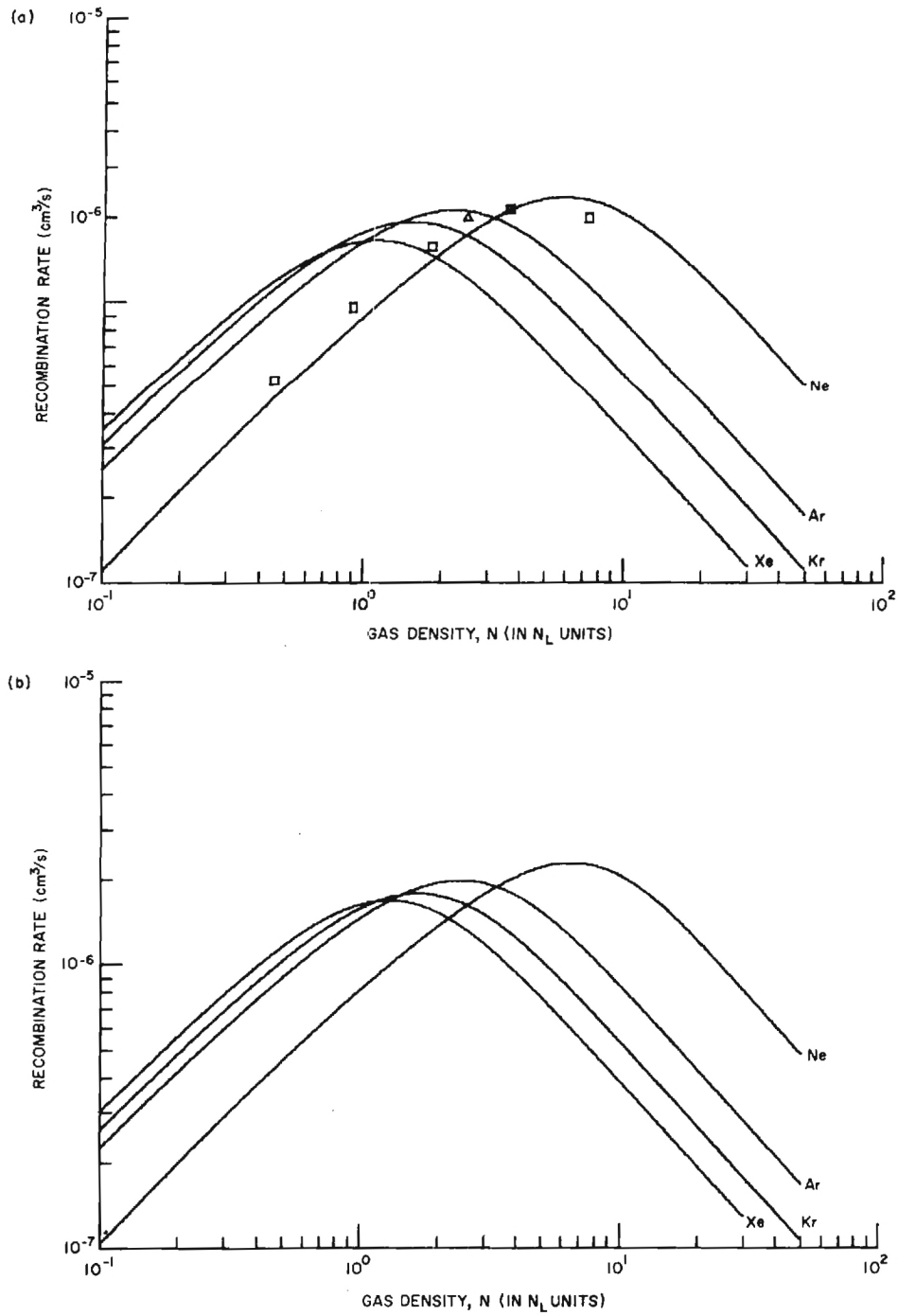

Fig. 3. Recombination rates for (a) Xe^+–Cl^- and (b) Xe_2^+–Cl^- in various gases (Ne, Ar, Kr, Xe). Monte Carlo results: (Bardsley and Wadehra, 1980) for Ne. △ (Bates, 1980c) for Ar.

at 300 K. Experimental mobilities (Ellis *et al.*, 1978; Johnsen and Biondi, 1979) were used for K_i and for determination (Flannery, 1972) of the mean free paths λ_i. According to Section III.C and to Flannery (1981b), little reduction to α is expected as $N^{\pm}$ is increased to as high as 10^{12} cm^{-3} of interest to gas lasers.

While the recombination process in principle populates all the excited molecular states, the branching ratio to the *B*, *C*, and *D* lowest excited manifold is effectively unity, since these states are the only ones with strong ionic character at intermediate nuclear separations and are well separated from other covalent states. Also the enhancement of mutual neutralization (Bates, 1979) as N is raised past $\sim\frac{1}{2} N_L$ is, for rare-gas halide systems, expected to be small in comparison with the three-body rates, since the ionic and covalent potentials of the (Rg*–F, Cl) systems occur at rather large separations (Flannery, 1979) with the possibility of abnormally small ($\sim 10^{-8}$ cm^3/s) Landau–Zener rates for mutual neutralization in the absence of third bodies (see also Bates, 1981b; Whitten *et al.*, 1982). For the rare-gas molecular ions, dissociative electron transfer (Flannery, 1979)

$$[Rg_2^+ - F^-]^* \longrightarrow RgF^* + Rg \tag{86}$$

in the quasibound triatomic complex stabilizes the recombination and ensures access of the RgF* channel in contrast to the Rg_2F^* channel. Formation of Rg_2F^* requires confinement of the trajectory of F^- to the plane normal to the symmetry axis, since its stable configuration is triangular. The RgF* channel in (86) is therefore more probable than the Rg_2F^* channel (cf. Flannery, 1979).

Also shown in the figures are the results (X, □; Kr^+–F in Ar and Ne, respectively; △ for Xe^+–Cl^- in Ar) from Bates's universal plot (Bates, 1980c) and results (□: Xe^+–Cl^- in Ne; ○: Kr^+–F^- in Ar) from direct Monte Carlo simulation (Bardsley and Wadehra, 1980; Morgan *et al.*, 1980) pertinent to dilute ionization $N^{\pm} \sim 10^8$ cm^{-3}. The treatment of Morgan *et al.* (1980) for higher $N^{\pm}$, based on the direct use of the Debye–Hückel interaction, is invalid, and the results are incorrect over all gas densities (Section III, Bates, 1981a; Flannery, 1981b,c). The overall good agreement exhibited by the figures summarizes the current status of ion–ion recombination coefficients as a function of gas density N.

For the heavier systems K_i is dominated by the polarization ion–neutral attraction, so that the figures can be made universal (Bates, 1980c) for all temperatures T simply by relabeling the ordinate and abscissa axes as $(T/300)^{3/2}\,\alpha$ and $(300/T)^{3/2}\,N$, respectively.

The only new measurements of α performed since the work of Mahan and associates for the limit at low gas densities N (see Mahan, 1973; Flannery, 1972, for this and earlier work) and of McGowan (1967) for N up to $\sim N_L$($\sim$760 Torr) are those deduced from the flame experiments of Burdett

and Hayhurst (1979) at the low N limit, and those of Sennhauser and Armstrong (1977) and of Sennhauser *et al.* (1980). This latter group measured α for the recombination of NH_4^+ (n NH_3) clusters with Cl^- (n' NH_3) or O_2^- (n' NH_3) clusters in pulsed irradiated ammonia vapor at 296 K over the wide range of gas pressures between 10 and 1200 Torr. These are the first experiments from a given laboratory which span the important pressure range containing the maximum of α and that therefore exhibited the turnover of α in the region becoming controlled by diffusion, a region previously indicated by the combination of the separate measurements of McGowan (1967) for (O_4^+–O_2^-) in O_2 and of Mächler (1936) for unknown species in air. In addition, they monitored the variation with N of the sizes ($n, n' \sim 2$–6) of the clusters, a feature that renders difficult measurements of benchmark quality.

All the preceding measurements are in essential agreement with results obtained from either the exact low density limit of Bates and Flannery (1968) or from the Natanson-modified procedure of Bates and Flannery (1969) for α versus N. The more accurate treatments presented in Section II.A of this chapter should help improve the overall agreement.

V. Conclusion

In the previous full discussion of the subject (Flannery, 1976) we concluded then with the hope that further study would shed intrinsic understanding of ion–ion recombination associated with intermediate gas densities N since the limits to α at low and high N were thoroughly established. Since then the basic theoretical problem of α versus N has been solved (Flannery, 1982a), Monte Carlo codes have been developed (Bates and Mendaš, 1978b; Bates, 1980a,b; Bardsley and Wadehra, 1980), and transient densities and rates have been obtained (Flannery, 1982a). This present discussion has indicated the impressive gains achieved since 1976 in both theoretical and experimental understanding of a very complicated process. An outstanding problem of the variation of α with increased ion density $N^{\pm}$ due to an intense source of ionization remains, although Flannery (1981b,c; 1982a), Bates (1981a), more detailed Monte Carlo simulations in progress by Morgan, Whitten, and Bardsley, and the developments in the present chapter have indicated substantial progress in its basic understanding.

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† Note that the trapping radius differs here from that derived by Flannery (1978) whose condition for trapping is $T_f = T_i(1 - F_i) \leqslant \int_R^{R+\lambda} (\partial V/\partial R)\, dR$ where T_i, the kinetic energy of (1–2) relative motion before the (i–3) collision, is given by (10) and where $F_i = 2M_1M_2M_3(M_1 + M_2 + M_3)/(M_1 + M_2)^2(M_i + M_3)^2$ to yield $\delta_i = F_i/(1 - F_i)$ in (12). Wadehra and Bardsley here assume T_f the kinetic energy of (1–2) relative motion after the (i–3) collision is $\frac{3}{2}kT + (1 - F_i)\int_R^{R-\lambda} (\partial V/\partial R)\, dR$, which therefore is assumed to remain always greater than its thermal value to give $\delta_i = F_i$. Note also that δ_i can, however, be now chosen as in Section II.B so as to reproduce at low N the exact low density results (Flannery, 1980, 1981a), a preferable procedure.

Appendix B

"Comment on Closed Form Solution of the Generalized Debye-Smoluchowski Equation", published in Physical Review Letters 49 (1982) 1681.

In this Appendix, the analytical formulae previously derived by Flannery (in the previous full report for 1981 and in Physical Review Letters 47 (1981) 163-166) for the recombination rate at all times are shown to yield the long-time transient recombination rate as obtained by an approximate method of Magee and Tayler (J. Chem. Phys. 56 (1972) 3061).

The required long-term transient behavior can be easily extracted from the analytical formulas of Flannery[1,2] as follows. In terms of the transformed separation[1,2]

$$\bar{R} = [\int_R^\infty \exp(V/kT) R^{-2} dR]^{-1} \quad (1)$$

and the diffusion coefficient D, the Debye-Smoluchowski equation for a general interaction $V(R)$ is exactly [Eq. (8), Ref. 1]

$$\partial \bar{n}(\bar{R},t)/\partial t = D(d\bar{R}/dR)^2 \nabla^2 \bar{n}(\bar{R},t) \quad (2)$$

and the required number density n is $\bar{n}\exp(-V/kT)$. By Laplace transformation of (2), the *exact* solution n at all R is given by Eq. (20a) of Ref. 1 with $(\bar{\chi},\bar{\Omega})$ replaced at long times by

$$\chi_l = (\alpha_{RN}/\alpha_\infty)S\sqrt{\tau}/\bar{S}, \quad \Omega_l = (\bar{R}-\bar{S})/2S\sqrt{\tau}, \quad (3a)$$

where τ is Dt/S^2 in terms of the sink radius S, and by

$$\chi_s = \chi_l (d\bar{R}/dR)_S, \quad \Omega_s = (R-S)/2S\sqrt{\tau} \quad (3b)$$

at short times. In (3a), the steady-state rate α_∞ is $\alpha_{RN}\alpha_{TR}/(\alpha_{RN}+\alpha_{TR})$ in terms of the reaction rate α_{RN} at S and the transport rate α_{TR} ($\equiv 4\pi D\bar{S}$) to S. From Eqs. (3a) and (3b) which are exact for all R at short and long times, respectively, $\chi_s = \bar{\chi}(S)$, and $\chi_s = \chi_l = \bar{\chi}$ when $d\bar{R}/dR$ can be taken as unity.

The transient rate of recombination, $\alpha_{RN} n(R,t)/N^- \exp(-V/kT)$ evaluated at S, is [Eq. (22a), Ref. 1]

$$\alpha(t) = \alpha_\infty[1 + (\alpha_{RN}/\alpha_{TR})\exp\chi^2 \operatorname{erfc}\chi] \quad (4)$$

which at short times (with $\chi = \chi_s$) reduces to the *exact* expression Eq. (24a) of Ref. 1 and at long times (with $\chi = \chi_l$) tends to the required *exact* long-time limit,

$$\alpha(t) \to \alpha_\infty[1 + (\alpha_\infty/\alpha_{TR})(S^2/\pi Dt)^{1/2}]. \quad (5)$$

The steady-state limit α_∞ is independent of χ. Equation (4) with Eqs. (3a) and (3b) reproduces the exact numerical solutions[3] for a Coulomb attraction to a very high degree of accuracy (e.g., to well within $\mp 3\%$ for $S \geq \frac{1}{2}e^2/kT$ and $\alpha/\alpha_{TR} \leq 0.5$ *at all times*). Corresponding formulas for the density $n(R,t)$ yield similar accuracy.

The long-time expression (5) is identical to that derived[4] by the method of "matched perturbation solutions," and is applicable all the way from the (low-density) reaction-limited regime ($\alpha_{TR} \gg \alpha_{RN}$) to the (high-density) diffusional-drift regime ($\alpha_{TR} \ll \alpha_{RN}$). The asymptotic (steady-state) rate remains preserved in time while the $t^{-1/2}$ long-time transient rate becomes suppressed in the reaction-limited regime at low gas densities when $\alpha_\infty \approx \alpha_{RN} \ll \alpha_{TR}$.

Equation (4) with $\chi = \bar{\chi}$ of Ref. 1 is valid over *all* times at all R which satisfy constant (unit) $(d\bar{R}/dR)$ appearing explicitly in

$$\left[\frac{\partial n'(\bar{R},t)}{\partial \bar{R}}\right]_t = \left[\frac{\partial n'(\bar{R},\bar{\tau})}{\partial \bar{R}}\right]_{\bar{\tau}} + \frac{d}{d\bar{R}}\left(\frac{d\bar{R}}{dR}\right)^2 \left[\frac{\partial n'(\bar{R},\bar{\tau})}{\partial \bar{\tau}}\right]_{\bar{R}} t, \quad (6)$$

where $\bar{\tau} \equiv (d\bar{R}/dR)^2 t$. Thus $\bar{\chi} = \chi_s = \chi_l$. Under this assumption consistently adopted in Eqs. (6) and (26) of Ref. 1, with $\bar{D} = D$, the exact long-time result (5) is again reproduced and the (B/A) ratio[4] is now unity.

For a pure Coulomb attraction $[V/kT = -1/R(\text{n.u.})$ where 1 natural unit (n.u.) is $e^2/kT]$, then $d\bar{R}/dR$ is 0.61, 0.80, 0.88, 0.92, 0.98, 0.995, and 0.999 at $R(\text{n.u.}) = 0.4$, 0.6, 0.8, 1, 2, 4, and 8, respectively. Thus (4) with $\bar{\chi}$ is effectively exact at all times for $R(\text{n.u.}) \gtrsim 1$ and, with χ_s and χ_l, is not only exact at all R for short and long times, respectively, but reproduces the exact numerical solutions quite accurately at all times (for $S \gtrsim \frac{1}{2}$ n.u. and $\alpha_\infty/\alpha_{TR} \leq 0.5$).

The existence of a simple analytical formula as (4) and corresponding n capable of this high numerical accuracy is quite advantageous and valuable, especially since there are as yet no simple transient solutions even for a specified V. It yields (a) the *exact* short-time and long-time transients for all gas densities (from the reaction-limited to transport-limited regimes), (b) the steady-state limit for all R, (c) the *exact* solution at all times t for all R which satisfy $d\bar{R}/dR \approx 1$, and (d) the exact solution at all t in the limit of weak interaction $V \ll kT$ for all R.

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Appendix C

Thermal Collisions of Rydberg Atoms with Neutrals, published in J. Phys. B: At. Molec. Phys. 15 (1982) 3249-3256.

In this Appendix, various criteria for validity of application of the impulse approximation to A-B($n\ell$) collisions are examined. The weak-binding and quasi-classical conditions are discussed. A connection between classical momentum and angular momentum changes is developed.

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Comments on 'Thermal collisions of Rydberg atoms with neutrals'

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Abstract. Various comments by Matsuzawa on validity criteria for application of the impulse approximation to A–B(n, l) collisions are examined and are shown to be without basis. The weak-binding and quasi-classical conditions are discussed and a connection between classical momentum and angular momentum changes is developed.

1. Introduction

A recent letter by Matsuzawa (1981) made several comments on the validity criteria of Flannery (1980a, b) for application of the impulse approximation to collisions between Rydberg atoms and neutral particles. In this paper we examine these comments and show that the arguments of Matsuzawa are not substantiated by the assumptions in the customary impulse approximation (IA) (see e.g., Goldberger and Watson (1964) to be referred to as GW). In support of this, we raise in § 2 and discuss in §§ 3–5 the various points of disagreement with Matsuzawa (1981). From the outset, it is worth mentioning that construction of rigorous criteria for validity of the IA is difficult but those derived by Goldberger and Watson (1964), by Flannery (1980a, b) and herein are perhaps the most accurate and rigorous to date.

2. Various issues

(A) A key quantity in equation (2) of Matsuzawa (1981) which is basic to his derived criterion for validity of the IA does not agree with the final expression of GW, although the same initial expression of GW was adopted. Matsuzawa's subsequent discussion of this validity criterion must then be viewed with some reservation since the derivation of the error estimated by GW and adopted by Flannery (1980b) is correct.

(B) Application of the IA to collisions involving arbitrarily small momentum changes still remains invalid (Flannery 1980a, b, Cheng and van Regemorter 1981) in disagreement with Matsuzawa.

(C) The impulse approximation to high-energy *neutral–neutral* elastic scattering (incorrectly) yields a zero differential cross section for scattering in the forward direction. Matsuzawa implies that the IA can correctly describe high-energy neutral–neutral forward scattering, a stand which is also inconsistent with (B) above.

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(*D*) That the IA description of small momentum changes is invalid has certain implications for angular momentum changes.

(*E*) Inelastic cross sections calculated from the customary IA (which is based 'on-the-energy-shell' collisions with the Rydberg electron e) cannot exceed the limit provided by all kinds of electron–projectile collisions (Flannery 1980b). Cross sections obtained by Matsuzawa from further (non-unitarised) approximations (Born) to the IA greatly exceed this limit.

(*F*) Can the core B^+ exercise any important effect in angular momentum l-mixing in A–B(n) thermal collisions as suggested by Flannery (1980a, b) and by Hahn (1982)? Recent experiments (Boulmer *et al* 1981a, b) on collisional depopulation via n-changing collisions, and direct numerical Monte-Carlo classical simulations (Lane and Preston 1982) of the ionisation of Rydberg atoms by thermal dipole molecules indicate that core effects are important for n changes. Or can one always *ad hoc* neglect core effects in l changes alone as asserted by Matsuzawa?

An important seventh point raised by Flannery (1980b) concerns the use in all IA treatments so far of l-changing thermal collisions (as in e.g., Matsuzawa 1979) of on-the-energy-shell (e–A) collisions which, although valid at high energies may involve error particularly for the thermal collisions under discussion. The above six points relevant to A–B(n) collisions are now amplified in §§ 3–5.

3. Validity criteria

In the basic IA to A–B(n) *inelastic* collisions energy and momentum changes originate from a collision between the Rydberg electron 1 which is assumed free and the incident projectile A labelled 3. The binding interaction V_{12} of 1 to the spectator B^+ core 2 is ignored except insofar as it generates the velocity distributions appropriate to the initial and final quantal states $\phi_n(\boldsymbol{R}_{12})$ of the B(n) system. *Elastic* A–B(n) collisions in the IA originate from e–A collisions (on and off the energy shell) and from B^+–A collisions which are described by Born's approximation (cf Flannery 1980b, equation (A.10)).

(*A*) *Weak binding and quasi-classical conditions.* Denote the speeds of particles i (=1, 2, 3) relative to the (1–2) centre of mass by v_i, the masses by M_i and let v_{ij} be the relative speed of i and j with reduced mass M_{ij}. The working equations basic to validity of the impulse approximation are equation (30a) on p 687 and equation (31) on p 690 of Goldberger and Watson (1964), referenced as GW, for each of the two distinct cases (a) of *weak binding* when the incident kinetic energy of A–B(n) relative motion is much greater than $|\varepsilon_n|$, the binding energy of the Rydberg electron to B^+, and (b) of a *quasi-classical* interaction V_{12} between 1 and 2 considered to have a slow variation. For the former case of *weak binding*, GW show that

$$\frac{f_{13}}{\lambda\!\!\!^{-}_{\rm rel}}\frac{\Delta E_{\rm c}}{\hbar}\left(\frac{\hbar}{E_{\rm rel}}+Q\right)\ll 1 \qquad (1a)$$

where f_{13} is the amplitude for free (1–3) scattering with time delay Q. The reduced wavelength $\lambda\!\!\!^{-}_{\rm rel}$ and the kinetic energy $E_{\rm rel}$ of (1–3) relative motion are $\hbar/(M_{13}v_{13})$ and $\frac{1}{2}M_{13}v_{13}^2$, respectively. When $v_3 \gg v_1$, then $\lambda\!\!\!^{-}_{\rm rel}E_{\rm rel}$ in (1a) equals $\lambda\!\!\!^{-}_3E_3$, where $\lambda\!\!\!^{-}_i$ is $\hbar/M_iv_i$ and E_i is $\frac{1}{2}M_iv_i^2$, which actually appears in expression (30a) of GW because of their assumption ($v_3 \gg v_1$). When $v_3 \ll v_1$, then $\lambda\!\!\!^{-}_{\rm rel}E_{\rm rel}$ reduces to $\lambda\!\!\!^{-}_1E_1$. According

to GW, ΔE_c in (1*a*) is the energy or level shift $\langle(\phi_n(\boldsymbol{R})|V_{12}(R)|\phi_n(\boldsymbol{R})\rangle$ of 1 due to the core interaction V_{12} and *is not* the variation of V_{12} over the range of the Rydberg electron 1–projectile 3 interaction as asserted by Matsuzawa (1981). When $f_{13} \sim \lambda_{rel}$ then, for $v_3 \gg v_1, E_3 \gg |\varepsilon_n|$ in accord with intuition. The origin of Matsuzawa's definition is not at all clear.

For the case of *quasi-classical* V_{12}, Goldberger and Watson evaluate the full commutator ($[R, (1/d_0)\mathcal{T}]$ in their notation, p 686) and assume that the (1–3) scattering interaction is physically independent of V_{12} with the eventual result that

$$\frac{f_{13}}{\lambda_{rel}} \frac{\hbar^2}{2M_1} \langle \nabla_R^2 V_{12}(R)\rangle \tau_c^2 = \frac{f_{13}}{\lambda_{rel}} \frac{\hbar^2}{2M_1} \frac{\langle V_{12}\rangle}{\mathcal{R}_{12}^2} \left(\frac{\hbar}{E_{rel}} + Q\right)^2 \ll 1 \tag{1b}$$

where τ_c is the collision time, $\mathcal{R}_{12}$ is the range of the binding interaction, and $\langle\ \rangle$ denotes an average over the initial electronic state ϕ_n. The quasi-classical condition (1*b*) can be satisfied when the weak-binding condition (1*a*) is violated. Note that it is (1*b*) and not (1*a*) which illustrates the natural validity of the impulse approximation for a constant interaction V_{12}.

Matsuzawa (1981) does not distinguish between the above two cases and he asserts that ΔE_c in (1*a*) is $|\nabla V_{12}|\mathcal{R}_{13}$, where $\mathcal{R}_{13}$ is the effective range of the (1–3) interaction in disagreement with Goldberger and Watson (1964). Note that $\mathcal{R}_{13}$ via the collision time $t_c \sim \mathcal{R}_{13}/v_{13}$ has already appeared in both (1*a*) and (1*b*) by way of $(\hbar/E_{rel} + Q)$, irrespective of ΔE_c. The argument based on Matsuzawa's interpretation must therefore be viewed with some reservation since the method of derivation of his equation (2) is somewhat obscure.

Since the interactions of 1 and 3 with the core 2 are switched off (except at asymptotic times when V_{12} is invoked to generate the initial and final states $\phi_{nl}(\boldsymbol{R})$), it is apparent that energy is imprecise to within ΔE_c. Thus, the cross section σ_{13} for (1–3) scattering must not exhibit too rapid a variation with energy (Condition *A* of Flannery 1980a); otherwise in the words of the originators (Chew and Wick 1952, p 637) of the impulse model, 'the whole method is meaningless' since the situation for which σ_{13} rapidly varies within imprecision ΔE_c is alien to the impulse treatment which, in principle, cannot handle such resolution. Resonances with width $\Gamma \leq \Delta E_c$ therefore, may be excluded because of conditions (1*a*, *b*) on the delay time Q via the rapid energy variation of the cross section σ_{13} in the neighbourhood of resonant energy.

(*B*, *C*) *Momentum change condition.* Condition *B* of Flannery (1980a) is concerned with the external momentum change P suffered in an (A–e) impulsive collision. Since the (e–B^+) interaction V_{12} is switched off during the (e–A) encounter, P is meaningful only when it is very much greater than the imprecision in momentum, i.e. in the neglected momentum imparted internally to e by V_{12} during the collision time τ_c so that,

$$P \gg \int_{\tau_c} F_{12}\, dt \approx |\langle\phi_{nl}|-\nabla V_{12}|\phi_{nl}\rangle|\tau_c \tag{2}$$

as in equation (2*a*) of Flannery (1980a) and in Cheng and van Regemorter (1981) (see equation (39)). Quasi-elastic collisions which therefore involve aribtrarily small momentum changes P are not well described by the impulse approximation, in contrast to the view held by Matsuzawa (1981). Moreover, even at high energy, *elastic neutral–neutral scattering* in the forward direction ($P \sim 0$) is not accurately described by the impulse approximation. At high energies, the standard impulse approximation reduces to the Born approximation for A–B(n) scattering (Mott and Massey 1965).

The Born cross section for *neutral–neutral* elastic scattering in the forward direction ($P = 0$) is identically zero (see analysis and both figures 1 of Flannery and McCann (1974a, b) where it is shown that the contributions from 1–3 and 2–3 collisions cancel) in contrast to more elaborate *unitarised* treatments (Flannery and McCann 1974a, b). As noted by Flannery and McCann (1974b), this inherent defect of Born's approximation is attributable to lack of conservation of probability. The resulting error is minimised, but is never removed, at high energies when the violation is confined to an ever-decreasing *angular region* about the forward direction. Since the impulse and Born treaments are identical in the high-energy limit, the impulse approximation does not furnish a correct description of *forward elastic high-energy* neutral–neutral scattering, in disagreement with Matsuzawa (1981) but will, of course, provide accurate integral cross sections since the relative importance of forward scattering (zero momentum change P) is largely diminished. Further, the use of the averaged force F_{12} in inequality (2) is consistent with the use in the IA of the full momentum amplitudes $g_i(\boldsymbol{k}_i)$ which can be obtained from the microcanonical classical distribution (Mapleton 1966) which assumed that all elements of phase space are equally populated. Even when the instantaneous force e^2/R_{12}^2 is used, the essential argument remains unaffected.

4. Angular momentum change

(D) Condition (2) for the change in linear momentum has some bearing to ($nl \to nl'$) transitions which involve a change in angular momentum but no internal energy change. In the impulsive encounter the $e\text{–}B^+$ separation $\boldsymbol{R}_{12}$ is fixed, the internal energy E_i ($\equiv T_i - e^2/R_{12}$) remains unaffected provided the initial kinetic energy T_i ($=\frac{1}{2}M_{12}v_{12}^2$) equals T_f, the final kinetic energy, and the classical angular momentum squared changes from

$$L_i^2 = 2M_{12}T_iR_{12}^2(1-\cos^2\theta) \qquad \cos\theta = \hat{\boldsymbol{R}}_{12}\cdot\hat{\boldsymbol{v}}_1 \tag{3a}$$

to

$$L_f^2 = 2M_{12}T_iR_{12}^2(1-\cos^2\alpha) \qquad \cos\alpha = \hat{\boldsymbol{R}}_{12}\cdot\widehat{(\boldsymbol{v}_1' - \boldsymbol{v}_2)} \tag{3b}$$

where $\boldsymbol{v}_2$, the velocity of the core, is $(-M_1\boldsymbol{v}_1/M_2)$ which can be taken to be effectively zero. With the initial velocity $\boldsymbol{v}_1$ of the Rydberg electron directed along the polar axis, and with the electron–core separation $\boldsymbol{R}_{12}$ fixed in the XZ plane, then the velocity of the Rydberg electron 1 after the collision is $\boldsymbol{v}_1'(v_1', \psi, \phi)$ so that

$$\cos\alpha = \cos\theta\cos\psi + \sin\theta\sin\psi\cos\phi \tag{4}$$

where (ψ, ϕ) are the polar and aximuthal angles of scattering.

Hence L_i^2 ranges from $L_{\max}^2$, its maximum value $2M_{12}T_iR_{12}^2 \approx [(n-1)\hbar]^2$, for circular orbits ($\theta = \frac{1}{2}\pi$), to zero for highly eccentric orbits ($\theta = 0$). Thus, the change

$$\Delta L^2 = L_f^2 - L_i^2 = L_{\max}^2[(\cos^2\theta - \sin^2\theta\cos^2\phi)\sin^2\psi - \tfrac{1}{2}\sin 2\theta\sin 2\psi\cos\phi]$$

$$\to \begin{cases} L_{\max}^2\sin^2\psi & \theta \sim 0 \quad \text{(low initial } l\text{)} \\ -L_{\max}^2\sin^2\psi\cos^2\phi & \theta \sim \frac{1}{2}\pi \quad \text{(high initial } l\text{)} \end{cases} \tag{5}$$

can be very large for an initial high n state. Since $v_1 \gg v_3$ for the thermal collisions

under consideration for most n of importance (see equation (3.11) of Flannery 1980b) then for isotropic scattering this change averaged over all (ψ, ϕ) is

$$\langle \Delta L^2 \rangle = \tfrac{1}{3} L_{\max}^2 (3\cos^2\theta - 1) \to \begin{cases} \frac{2}{3} L_{\max}^2 & \text{low initial } l \\ -\frac{1}{3} L_{\max}^2 & \text{high initial } l \end{cases} \tag{6}$$

which is always large $\sim L_{\max}^2$, and constant depending only on the initial n value (see also Flannery and McCann 1979, 1980). From (5), small angular momentum changes can occur for low initial l only for forward or backward scattering ($\psi \sim 0, \pi$). The forward direction ($\psi \sim 0$) involves small changes in linear momentum which, in principle, from (2) cannot be handled adequately by the IA. Note, however, that small ΔL can occur via off-the-energy-shell encounters when $T_i \neq T_f$ or, in general, for $nl \to n'l'$ transitions which in addition involve a change in internal energy. Also note for highly eccentric orbits ($\theta \sim \frac{1}{2}\pi$) that there is a substantial probability for close encounters between e and its B^+ core such that the interaction of the projectile A with the B^+ core during an (e–A) collision is inevitable—a feature not acknowledged by IA.

The change ΔL for low and high initial l can alternatively be written by the introduction of the momentum change P ($\equiv 2M_{12}v_{12}\sin\frac{1}{2}\psi$) in (5) as

$$\Delta L^2 \to \begin{cases} P^2 R_{12}^2 \cos^2 \tfrac{1}{2}\psi & \text{low initial } l \qquad (7a) \\ -P^2 R_{12}^2 \cos^2 \tfrac{1}{2}\psi \cos^2\phi & \text{high initial } l \qquad (7b) \end{cases}$$

which shows directly that small ΔL for low initial l can orginate both from small P and from backward scattering ($\psi \sim \pi$) where P is greatest. Because of (2), only this latter region of large P can adequately be described by the customary IA. The IA is adequate for small ψ only when $\Delta L \approx PR_{12}$ is much larger than the limit obtained (by Flannery 1980a, b) by inserting (2) in (7a). It may happen, however, that integration over that angular region inadequately described by the IA for small l changes could yield a result which is either negligible or which (fortutiously) may agree with more accurate results.

5. Plane-wave IA and core effects

(E) The picture basic to the impulse approximation of A–B(n) collisions is that inelastic processes occur via a collision between the mono-energetic projectile A and a Rydberg electron with momentum $\boldsymbol{k}_1$ smeared out with amplitude $g_i(\boldsymbol{k}_1)$ determined from its initial orbital $\phi_n(\boldsymbol{r})$. Thus, *the rate for any inelastic process in this picture* must be limited by the rate of all types of (e–A) collisions, i.e. the cross section for A–B(n) inelastic collisions must satisfy

$$\sigma \leqslant \frac{1}{v_3} \int |g_i(\boldsymbol{k}_1)|^2 v_{13} \sigma_{13}^{\mathrm{T}}(v_{13})\, \mathrm{d}\boldsymbol{k}_1 \tag{8}$$

where v_1 and v_3 are the respective speeds of the Rydberg electron and of A both relative to the centre of mass of B(n) and where σ_{13}^{T} is the integral cross section for all elastic and inelastic (e–A) collisions at relative speed v_{13}. Due to condition (2), derivation of (8) via use of the optical theorem on the IA amplitude is inappropriate.

The above result (8) can be established by noting that the quantal IA, under the assumptions of on-the-energy-shell (1, 3) encounters and of a plane wave for the final

state of the Rydberg electron exactly reduces under transformation (see § 4 of Flannery 1980b) to the semi-quantal (SQ) treatment of Flannery (1970, 1973). This SQ treatment is based on the initial expression

$$d\sigma = \frac{1}{v_3} v_{13}\sigma(v_{13}, \psi)\, d(\cos\psi)\, d\phi\, \tfrac{1}{2} d(\hat{\boldsymbol{v}}_1 \cdot \hat{\boldsymbol{v}}_3) \tag{9}$$

for that contribution to the A–B(n) differential cross section which arises from 1–3 scattering in the (1–3) centre-of-mass frame with cross section $\sigma(v_{13}, \psi)$ per unit solid angle about (ψ, ϕ). On acknowledging the distribution $|g_i(\boldsymbol{k}_1)|^2$ in momentum of the Rydberg electron, we note that the upper limit to (9) is (8).

When a computed impulse cross section yields a result greater than (8), as in the case of Matsuzawa (1979), then indications are that Born-type approximations for $\sigma(v_{13}, \psi)$ which do not satisfy unitarity have been invoked within the IA or that a plane-wave final state yields an underestimate, an unusual occurrence, in general. The plane-wave IA cannot provide any additional contributions to the cross section over the limit specified by (8). Note at high impact energies, $v_3' \gg v_1$ and the limit (8) to A–B(n) collisions is simply the cross section σ_{13}^{T} for e–A collisions in accord with the free collision model of Dmitriev and Nikolaev (1963) adopted successfully by many authors (e.g., Victor 1969) for electron-loss calculations. The measured cross sections at thermal energies can, of course, exceed the impulse limit (8) which ignores off-the-energy-shell contributions from e–projectile collisions, various core effects and core distortion to the plane-wave final state, all of which may be important for quasi-elastic thermal collisions.

(*F*) The effect of the ionic core B^+ in l-mixing transitions in A–B(n) collisions raises interesting problems. Both Smirnov (1974) and Flannery (1980a, b) suggested that the ion core *could* make a significant contribution via a mechanism not included in the customary expression for the impulse approximation. In particular, Flannery (1980a) noted that the contribution to l-changing transitions arising from $A–B^+$ encounters *could be* dominant at energies where the Ramsauer–Townsend minimum is exhibited in e–rare-gas collisions. Hahn (1982) has recently shown that the distortion correction to l-changing collisions due to the $A–B^+$ interaction is large for intermediate values of $n \leqslant 20$ in l-changing collisions and that the effect on the t-matrix t_{23} for $A–B^+$ collisions through higher-order terms neglected in the customary impulse approximation can be very important. Lane and Preston (1982) have demonstrated via a direct numerical Monte-Carlo classical simulation that the core is very important in ionisation of Rydberg atoms (Ar(ns), $n \geqslant 30$) by thermal dipole molecules (as HCl). The physical mechanism introduced by Flannery (1980a, b) attempted to describe the overall effect of the higher-order (core) terms neglected in the customary IA. Hahn (1982) has since investigated these terms and his results are consistent with this mechanism.

There is at present no direct experimental evidence although experimental evidence on a related issue is mounting. Some indication is present in a recent experiment on excitational exchange of Rydberg levels in He(n)–He(1) collisions by Boulmer *et al* (1980) who found that the process is dominated by the interaction of the ionic He^+ core with He and proceeds at the charge exchange rate with the excited Rydberg electron remaining a spectator. Experiments (Kachru *et al* 1980) on collisional broadening of Rydberg levels show that the total cross section of all elastic, quasi-elastic, inelastic and superelastic collisions is affected greatly by interaction with the core. The relative amounts distributed between elastic and quasi-elastic collisions is

difficult to assess but quasi-elastic collisions could well be greatly affected (Hartmann 1981). Recent experimental data of Higgs *et al* (1981) for l changes in Xe(24f)–Ar, CO and N_2 collisions are consistent with the inclusion of core effects. Finally, Boulmer *et al* (1981a, b) have recently concluded that n changes in Na(ns)–Ar collisions originate primarily from interaction with the core for high $n \geqslant 20$.

Neither Matsuzawa (1981) who used an expression of Flannery (1980b, equation (5.24)), which is valid *only* in the high-energy A–B impulsive limit alien to the thermal collisions under discussion, or the recent calculations of Hickman (1981) which are based on a separated-atom picture have satisfactorily justified the neglect of core effects. In A–B(n) thermal collisions, the speed of the Rydberg electron is much greater than the $A–B^+$ relative speed such that a proper theoretical treatment must be based on some molecular approach (cf Janev and Mikajlov 1979) rather than on the separated-atoms approach of Hickman (1981). There is a difference between inserting the $A–B^+$ interaction in a treatment which does not include the full molecular collisional mechanism as in Hickman's work and a proper molecular treatment which provides the response of the Rydberg electron to the changing field of the quasi-molecular ionic complex.

Finally, it is worth noting that the remark of Matsuzawa (1981) concerning equation (5.6) of Flannery (1980b) is in error. As explained in the text (Flannery 1980b) this equation (5.6) pertains only to the Coulomb interaction in ion–charged-core collisions.

6. Conclusion

In conclusion, we have presented above six key points which do not agree with the comments of Matsuzawa (1981). The first five points (A)–(E) appear basic to correct interpretation of the impulse approximation, while the sixth point concerning core effects is outside the scope of the cusomary impulse approximation. While there is firm evidence in favour of core effects in collisional depopulation via n-changing collisions and in Rydberg ionisation by dipole molecules, detailed explanation of the role of the core in l-changing collisions still requires detailed theoretical study based on a full molecular approach (Janev and Mikalov 1979) or on a Monte-Carlo simulation (Lane and Preston 1982). A seventh and possibly important point raised by Flannery (1980b) concerns the tacit assumption of only 'on-the-energy-shell' encounters in the application by Matsuzawa (1979) of the IA to thermal l-changing collisions. The assumption, while valid in the high-energy limit, may not be appropriate to thermal quasi-elastic collisions.

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Appendix D

Theory of Rydberg Collisions with Electrons, Ions and Neutrals published in Rydberg States of Atoms and Molecules (Cambridge University Press, 1982) Chapter 11, pages 393-453.

In this Appendix, we have provided a comprehensive and unified formulation of theory suitable for the calculation of cross sections for collisions of atoms initially excited with electrons, ions and neutrals. In so doing, new material has been developed and conditions for validity of the various methods suggested become more apparent. The main contents are as follows:

1. Classification of Treatments for Rydberg Collisions.
2. Quantum Theory of Rydberg Collisions.
3. Semiclassical Theory of Rydberg Collisions.
4. Quantal-Classical Correspondences.
5. Quantal Impulse and Semiquantal Methods.
6. Monte Carlo Procedures.
7. Semiempirical Electron-Impact Cross Sections.
8. Summary.

11

Theory of Rydberg collisions with electrons, ions, and neutrals

M. R. FLANNERY

11.1. Classification of treatments for Rydberg collisions

In this chapter we shall present theory suitable for the description of collisions between Rydberg atoms B(n) in quantum state n and electrons, ions, and neutrals denoted, in general, by A, with detailed emphasis on electron impact. The various methods fall quite naturally into three broad, overlapping, classifications - quantal, semiquantal-semiclassical, and classical - each characterized by certain properties peculiar to the collision and by certain validity criteria satisfied by the particular process under consideration. Various quantal-classical combinations within the continuous classification can be used to describe both the relative A-B(n) *external* motion in the continuum and the *internal* bounded motion of the Rydberg electron e attached to its parent core B^+ in state n, such that the overall treatment is hybrid in nature.

The term *semiclassical* is used in the sense of the JWKB approximation to external and internal wave functions, and *semiquantal* refers to an impulse treatment wherein the Rydberg electron-projectile A scattering is described by full quantal scattering technology and the associated energy and momentum changes are prescribed by classical mechanics. This semiquantal method[1] is equivalent[2] to the full quantal impulse approximation with a plane-wave for the final state of the Rydberg electron.

As n is increased, the Rydberg electron eventually behaves as a classical particle in the sense that it becomes increasingly localized in phase space, where the quantal imprecisions Δr_n and Δv_n associated with its position r_n relative to the core B^+ and with its orbital speed v_n about the core are $\ll r_n$ and v_n, respectively. Quantal characteristics remain as exhibited, for example, by radio-frequency line emissions between neighboring levels,[3] with n as high as ~ 250. Because electronic quantal wave functions for bound excited states tend, in the limit of high n, to semiclassical JWKB wave functions, which lead naturally to the Bohr-Sommerfeld quantization rule and hence to the Bohr correspondence principle for line emission and absorption between highly excited levels (Sects. 11.4a and 11.4b), the essential quantum mechanics underlying internal motion is preserved and the correct quantal-classical connection or correspondence is provided by semiclassical internal wave func-

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tions. Also, for heavy-particle collisions at impact energies above the well depth of A–B(n) attraction and for high-energy electron impact, the more familiar semiclassical description of external relative motion is accurate. Cross sections, transition amplitudes, etc., require knowledge of matrix elements M_{ij} of some kernel M (such as the scattering operator and electrostatic interaction, for example) averaged over electronic wave functions for a given (i,j) pair of excited states i and j. Direct quantal evaluation of M_{ij} is laborious because each highly oscillatory quantal wave function (with $\sim n$ nodes for each direction) requires specification at more than n^3 points and is, apart from the end result, unrewarding. Semiclassical wave functions not only expose much beauty in the quantal–classical connection (Sect. 11.4e) but also lead directly to the Heisenberg correspondence principle (Sect. 11.4b), which expresses any general M_{ij} as the sth Fourier component ($s=|i-j| \ll i,j$) of M evaluated along a mean internal classical orbit $\mathbf{r}(t)$ for the Rydberg electron. This principle represents a very efficient and powerful method for evaluation of matrix elements with $i,j \gg s$.

Many kinds of A–B(n) collisions involve strong coupling between many states strongly connected to the initial and final states under consideration such that perturbation-based full quantal procedures developed originally with ground-state B in mind are, in general, unrealistic, except in the weak-coupling limit. For collisional transitions between strongly coupled neighboring or adjacent, equally spaced levels, the probability amplitudes for $n \rightarrow n'$ transitions can be exactly determined,[4-6] with the aid of Heisenberg's correspondence principle (or semiclassical internal wave functions) within a semiclassical description of the collision, to give what is termed the *equivalent oscillator theorem* (Sects. 11.4d and 11.4e) or, alternatively, the *strong-coupling correspondence principle*.[5] Although its one- and three-dimensional forms can be derived from several related avenues,[4-7] a new, direct, and rigorous derivation based on the action-angle representation will be presented in Sect. 11.4d. These amplitudes may then be inserted into an appropriate treatment (such as the semiclassical multichannel eikonal treatment[8] or the classical path treatment given in Sect. 11.3) for the collision cross section. Overall, semiclassical methods properly developed for Rydberg collisions are not alternatives to full quantal procedures; rather they provide the most efficient methods for application of quantum mechanics to A–B(n) collisions.

Application of purely quantal methods would prove too cumbersome in that the density of states for transitions between excited levels is too large for individual attention to each state. Only for scattering by a dipole in the weak-coupling limit can summation over the n^2 degenerate states associated with a given hydrogenic level n be carried out analytically. The standard quantal close-coupling (QCC) method, based on a perturbation expansion, is useful only when a limited small number of states are accessible (as in collisions that mix only the angular momentum states l of a given n). Also the standard difficulties associated with the convergence of partial cross sections for each par-

tial angular momentum L wave of relative motion would be considerably amplified over those evident for processes with atoms initially in ground states because, in e-B(n) collisions, the effect of the induced dipole is very strong and long range, and the cross section is, in general, dominated by scattering in the forward direction. This difficulty is greatly reduced in an impact-parameter representation of the scattering amplitude, as in the multichannel eikonal treatment[8] such that convergence is rapidly obtained. Use of a restricted atomic basis set, however, limits close-coupling procedures (whether quantal QCC or semiclassical SCC) to cases of weak coupling with the neglected states, a circumstance that becomes increasingly rare even for moderate values of n. For high n, the Rydberg target behaves more like two distinct scattering centers such that expansion in terms of functions that describe external relative motion distorted by the averaged atomic field is not the most effective or even desirable procedure for a limited basis set. For example, a product of Coulomb functions centered at the Rydberg electron e and its core B^+ is obviously a better zero-order choice for relative motion in ion or electron impact than is a plane wave distorted by the averaged atomic field.

A full quantal method more effective than any close-coupling (CC) procedure, QCC or SCC, in that it is not based on a perturbation expansion, has been developed specifically for A-B(n) collisions.[9] Here A moves in a field given, not by the static interaction averaged over the internal electronic motion, the basis of CC, but rather by the superposition of two strong (A-e and A-B^+) fields that remain essentially instantaneous when the speed v_n of the Rydberg electron about B^+ is very much less than the speed v_{AB} of relative motion of the projectile A. This combination reduces to the averaged field only for distant encounters (a weak-coupling situation). When the effect of the Rydberg core is neglected, this "fixed-center" quantal method (QFC) reduces (Sect. 11.2) to the quantal and semiquantal (or plane-wave) impulse approximations[2] and then to the Born first-order result in the limit of weak coupling. The classical binary-encounter method for charged-particle–atom collisions can then be deduced (Sect. 11.5) by assuming a plane-wave final electronic state and the Rutherford cross section for projectile–Rydberg electron scattering and by neglecting the momentum distribution of the Rydberg electron.

Collisional transitions between neighboring levels ($n, n' \gg |n-n'|$) demand strong coupling theories, such as the equivalent oscillator theorem (EOT) for the $n \to n'$ transition amplitudes within a semiclassical description of the cross section or the quantal fixed-center treatment for $nlm \to n'l'm'$ transitions. For adiabatic collisions (distant encounters) and sudden collisions (close encounters), EOT reduces to the Born and sudden approximations, respectively, to be used where and when appropriate.

For $n' \gg n$ and for ionization, the quantal and semiquantal impulse treatments[2] (Sect. 11.5) and the pure classical binary-encounter method are valid, provided that the energy and momentum changes are much greater than the energy and momentum imparted to the Rydberg electron by its parent core B^+

during the time of close collision. Classical Monte Carlo computer simulations,[10,11] based on a solution of the equations of motion for the three-body system, are effective and reliable for ionization.

Various classical–quantal correspondences and theories of charged-particle–Rydberg collisions were already discussed by Percival and Richards.[12] In this chapter we shall attempt to provide a comprehensive and unified formulation of collision treatments suitable for Rydberg collisions with electrons, ions, and neutrals. In so doing, new material will be developed and conditions for validity of each method will become more apparent. It will also become apparent that considerable power lies in solution of the problem in either the action-angle variable representation of quantum mechanics or the (perturbed) Hamilton–Jacobi equation of classical mechanics for the action S so as to yield a semiclassical wave function with its automatic built-in quantization, which is very natural for Rydberg states. The former procedure is very akin to the Heisenberg matrix formulation of quantum mechanics,[13,14] and the first part of the latter procedure awakens interest in various perturbative techniques,[15,16] based on the Hamilton–Jacobi equation, which were highly developed in connection with problems in celestial mechanics and which remained dormant after the introduction of quantum mechanics. The atomic bound problem[15] is simpler, in that only a discrete number of motions is selected by quantization from the whole continuum of classical solutions, and yet more difficult, in that the replusion between two electrons can be greater than or comparable to the force of attraction with the core, whereas the perturbation between two planets is extremely small in comparison to attraction with the sun.

11.2. Quantum theory of Rydberg collisions

11.2a. Close-coupling procedures

The wave function $\Psi(\mathbf{r}, \mathbf{R})$ for the scattering of a Rydberg atom A and some atomic or molecular species B by their mutual interaction $V(\mathbf{r}, \mathbf{R})$ at relative separation $\mathbf{R}$ and internal electronic coordinates $\mathbf{r}$ is, in their c.m. reference frame, the appropriate outgoing-wave solution of the stationary-state Schrödinger equation,

$$H\Psi \equiv \left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + H_0(\mathbf{r}) + V(\mathbf{r}, \mathbf{R}) \right] \Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \tag{1}$$

where μ is the reduced mass and E the total energy of the collision system. The internal structure of the isolated species with internal coordinates collectively denoted by $\mathbf{r}$ is described by the Hamiltonian H_0 with eigenenergies ϵ_n and eigenfunctions $\{\phi_n\}$ assumed as known solutions of

$$H_0(\mathbf{r})\phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r}) \tag{2}$$

such that, in terms of the wave number k_n for relative motion, the total energy

$$E = \epsilon_n + (\hbar^2 k_n^2/2\mu) \tag{3}$$

is constant for all channels n. The scattering solution of Eq. (1) can be expanded in terms of $\{\phi_n\}$ as

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n F_n(\mathbf{R})\phi_n(\mathbf{r}) \tag{4}$$

where the unknown F_n for the relative motion can be shown, with the aid of (2) and (3), to satisfy the standard set of coupled, three-dimensional, differential equations

$$[\nabla_{\mathbf{R}}^2 + K_f^2(\mathbf{R})]F_f(\mathbf{R}) = (2\mu/\hbar^2) \sum_{n \neq f} V_{fn}(\mathbf{R})F_n(\mathbf{R}) \tag{5}$$

where

$$K_f(\mathbf{R}) = [k_f^2 - (2\mu/\hbar^2)V_{ff}(\mathbf{R})]^{1/2} \tag{6}$$

are the *local* wave numbers for relative motion under the static interaction $V_{ff}(R)$, the diagonal elements of the matrix

$$V_{fi}(\mathbf{R}) = \langle \phi_f(\mathbf{r}) | V(\mathbf{r}, \mathbf{R}) | \phi_i(\mathbf{r}) \rangle_{\mathbf{r}} \tag{7}$$

The usual quantal procedure converts (5) via a partial-wave analysis to analogous sets of coupled one-dimensional equations that require solution for each conserved angular momentum quantum number L, the vector sum of internal and relative motions. This procedure is the standard quantal close-coupling method (QCC), exact in principle but limited in practice to situations that involve only a small number of internal states n and values $L \lesssim 10$–20, the number depending on both the impact energy and effective range of interaction. When the basis set is, however, limited to all $|lm\rangle$ angular momentum states appropriate to principal quantum number n remaining fixed, then the further quantal development from Eq. (5) by Arthurs and Dalgarno[17] for collisional–rotational transitions in molecules is directly applicable to $nl \rightarrow nl'$ transitions in Rydberg atoms (see Chap. 6) and is feasible at low thermal energies.

The general application of Eq. (5) when decomposed to the corresponding set of one-dimensional equations is plagued by slow convergence of the partial-wave expansion and becomes prohibitively difficult particularly for higher-energy Rydberg collisions involving changes in both n and l. Semiclassical close-coupling methods[8,18] (multichannel eikonal and orbital treatments in Sect. 11.3), based on initial approximation of the three-dimensional set of Eq. (5) to a set that can then be solved exactly in three dimensions without recourse to angular momentum decomposition of the relative motion, are extremely powerful for Rydberg collisions. Here, convergence of transition amplitudes in an "impact-parameter" representation (not necessarily purely

classical) is more rapidly achieved than in the angular momentum representation, and the methods can be applied to situations prohibitive to a pure QCC treatment, e.g., Rydberg collisions in general, particularly at higher impact energies.

Because electronic wave functions ϕ_n for higher n contain many oscillations (with n^3 nodes in three dimensions), direct evaluation of those matrix elements in Eq. (7) that enter in quantal and semiclassical close-coupling treatments is, in general, not feasible or even recommended. More effective methods (Sect. 11.4) based on the Heisenberg correspondence principle or on the use of semiclassical (hydrogenic) wave functions, represent powerful techniques.

However, an obvious disadvantage, i.e., the limited extent of the basis set (4) taken in practice, remains in all close-coupling treatments, whether quantal or semiclassical, of Rydberg collisions. With the aid of the Bohr and Heisenberg correspondences (Sect. 11.4b) for high-Rydberg atoms, transition amplitudes can, however, be obtained exactly in the semiclassical version under certain conditions. This exact solution is designated here as an equivalent oscillator theorem (Sect. 11.4d).

A second quantal approach, which bears no obvious relationship to close-coupling methods characterized by (5)–(7), has been developed specifically for Rydberg collisions and will now be outlined.[9]

11.2b. Scattering by a fixed two-centered Rydberg target

A useful quantal treatment specifically designed for collisions involving a range of excited states has been developed from the operator formalism of scattering to allow greater transparency than (5) to the inclusion of various important effects and to permit construction of the resulting expressions in a form suitable for effective and interesting approximations.[9] The Lippmann-Schwinger operator equation describing the outgoing scattering of two atomic collision partners by their mutual interaction V is, in terms of the Green's resolvent G and transition operator T for the collision, given by

$$\Psi_i^+ = \Phi_i + G_0^+ V \Psi_i^+ = \Phi_i + G^+ V \Phi_i = \Phi_i + G_0^+ T \Phi_i \tag{8}$$

in the center-of-mass system. The solution Ψ_i^+ of (1) with appropriate outgoing, spherically scattered waves can be written as

$$\Psi_i^+(\mathbf{r}, \mathbf{R}) = \phi_i(\mathbf{r}) \exp(i\mathbf{k}_i \cdot \mathbf{R}) + \iint d\mathbf{r}' d\mathbf{R}' G_0^+(\mathbf{r}, \mathbf{R}; \mathbf{r}', \mathbf{R}') V(\mathbf{r}', \mathbf{R}) \Psi_i^+(\mathbf{r}', \mathbf{R}') \tag{9}$$

The Green's function G_0^+ satisfies

$$(E_i - \mathcal{H}_0 + i\epsilon) G_0^+(\mathbf{r}, \mathbf{R}; \mathbf{r}', \mathbf{R}') = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{R} - \mathbf{R}') \tag{10}$$

and can therefore be expanded in terms of the complete set

$$\Phi_i(\mathbf{r},\mathbf{R}) = \phi_i(\mathbf{r})\exp(i\mathbf{k}_i\cdot\mathbf{R}) \tag{11}$$

which are free-particle eigenfunctions of $\mathcal{H}_0$ ($\equiv H-V$), i.e., (1) in the absence of the interaction V, to give

$$G_0^+(\mathbf{r},\mathbf{R};\mathbf{r}',\mathbf{R}') = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\sum_n \frac{\exp(ik_n|\mathbf{R}-\mathbf{R}'|)}{|\mathbf{R}-\mathbf{R}'|}\phi_n^*(\mathbf{r})\phi_n(\mathbf{r}') \tag{12}$$

By considering the asymptotic ($R\to\infty$) behavior of (12) in (9), the transition matrix T and associated scattering amplitude f_{if} can be defined with elements

$$\begin{aligned} T_{fi} = \langle\phi_f|T|\phi_i\rangle &= \langle\phi_f(\mathbf{r})\exp(i\mathbf{k}_f\cdot\mathbf{R})|V(\mathbf{r},\mathbf{R})|\Psi_i^+(\mathbf{r},\mathbf{R})\rangle \\ &= -(4\pi\hbar^2/2\mu)f_{if}(\mathbf{k}_i,\mathbf{k}_f) \end{aligned} \tag{13}$$

Because exact solutions to (8) for use in (13) do not, in general, exist, various methods for constructing the T matrix (or Ψ_i^+ and G^+), based on a perturbation expansion in the interaction V (assumed weak), give rise to close-coupling schemes (Sect. 11.2a) that are exact in principle but limited in practice to a restricted basis set. There is, however, another alternative that involves the approximation of G_0^+ in (12) with respect to k_n, rather than G^+ in (8) with respect to V. In Rydberg collisions at intermediate and high impact energies, for example, it is a good approximation to write $k_n \simeq k_i$ in (12), which reduces, with the aid of the closure formula

$$\sum_n \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{14}$$

for the complete set of internal target states to

$$G_0^+(\mathbf{r},\mathbf{R};\mathbf{r}',\mathbf{R}') = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\frac{\exp(ik_i|\mathbf{R}-\mathbf{R}'|)}{|\mathbf{R}-\mathbf{R}'|}\delta(\mathbf{r}-\mathbf{r}') \tag{15}$$

with the result that the integration over $\mathbf{r}'$ in (9) can be performed. Thus this closure approximation, *valid when the energy of the incident projectile is large compared with the internal energy-level spacings of the A–B system,* replaces the many-particle Green's function, in effect by the free-particle Green's function, with the result that the total scattering function is

$$\begin{aligned} \Psi_i^+(\mathbf{r},\mathbf{R}) &= \phi_i(\mathbf{r})\exp(i\mathbf{k}_i\cdot\mathbf{R}) \\ &\quad -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int d\mathbf{R}'\frac{\exp(ik_i|\mathbf{R}-\mathbf{R}'|)}{|\mathbf{R}-\mathbf{R}'|}V(\mathbf{r},\mathbf{R}')\Psi_i^+(\mathbf{r},\mathbf{R}') \end{aligned} \tag{16}$$

a form that suggests the following substitution:

$$\Psi_i^+(\mathbf{r},\mathbf{R}) = \phi_i(\mathbf{r})\chi_i^+(\mathbf{r},\mathbf{R}) \tag{17}$$

where the new function χ_i^+ satisfies the integral equation

$$\chi_i^+(\mathbf{r},\mathbf{R}) = \exp(i\mathbf{k}_i\cdot\mathbf{R}) - \frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int d\mathbf{R}'\frac{\exp(ik_i|\mathbf{R}-\mathbf{R}'|)}{|\mathbf{R}-\mathbf{R}'|}V(\mathbf{r},\mathbf{R}')\chi_i^+(\mathbf{r},\mathbf{R}') \tag{18}$$

This equation describes the potential scattering of a fictitious projectile of original wave number k_i by a fixed, multicentered, electrostatic interaction $V(\mathbf{r},\mathbf{R})$. The transition matrix (13) for the A–B collision is therefore

$$T_{fi} = \langle\phi_f(\mathbf{r})\exp(i\mathbf{k}_f\cdot\mathbf{R})|V(\mathbf{r},\mathbf{R})|\phi_i(\mathbf{r})\chi_i^+(\mathbf{r},\mathbf{R})\rangle \tag{19}$$

which may be alternatively written as

$$T_{fi} = \langle\phi_f(\mathbf{r})|T_e(\mathbf{k}_i,\mathbf{k}_f;\mathbf{r})|\phi_i(\mathbf{r})\rangle_{\mathbf{r}} \tag{20a}$$

where

$$T_e(\mathbf{k}_i,\mathbf{k}_f;\mathbf{r}) = \langle\exp(i\mathbf{k}_f\cdot\mathbf{R})|V(\mathbf{r},\mathbf{R})|\chi_i^+(\mathbf{r},\mathbf{R})\rangle_{\mathbf{R}} \tag{20b}$$

is the T matrix for scattering by the fixed structureless potential $V(\mathbf{r},\mathbf{R})$ and is evaluated both on $(k_i=k_f)$ and off $(k_i\neq k_f)$ the energy shell. Thus (20a) emphasizes directly the unique role of elastic scattering in inelastic collisions and involves, as the only unknown (20b) or, alternatively, the full solution to the equation

$$[-(\hbar^2/2\mu)\nabla_{\mathbf{R}}^2 + V(\mathbf{r},\mathbf{R})]\chi_i^+(\mathbf{r},\mathbf{R}) = E_i\chi_i^+(\mathbf{r},\mathbf{R}), \qquad E_i = \hbar^2k_i^2/2\mu \tag{20c}$$

subject to the usual outgoing scattering condition. Note that all the information obtained in general by numerical integration of (20c) is used in T_{fi}. The scheme is therefore efficient in that the work entailed in the solution χ_i^+ to (20b) is not redundant, as opposed to other methods based on perturbation series for which a solution is integrated out from the origin in an effort to obtain only its asymptotic behavior. The full knowledge of χ_i^+ for all $\mathbf{R}$ is, of course, associated with the fact that the full T matrix (20b), with elements on and off the energy shell, is required.[9] Moreover, once $\chi_i^+(\mathbf{r},\mathbf{R})$ is obtained for a given scattering system, then it is preset for examination of all transitions within the system, i.e., χ_i^+ needs to be determined only once over the effective $(\mathbf{r},\mathbf{R})$ range of a given system.

Thus the inelastic scattering of composite structures is reduced to the solution of elastic scattering by fixed centers of potential, which are, in general, multiple. For A–B(n) collisions,

$$V(\mathbf{r},\mathbf{R}) = V(\mathbf{r}_1,\mathbf{r}_3) = V_{13}(\mathbf{r}_{13}) + V_{C3}\left(\mathbf{r}_3 + \frac{M_1}{M_1+M_2}\mathbf{r}_1\right) \tag{21}$$

where the Rydberg electron, its core C, and the projectile are denoted by 1, 2, and 3, respectively, and the position vector of each particle $\mathbf{r}_i$ is relative to the center of mass, which may be taken as the core of the Rydberg atom, except when electronic transitions arise from A–C encounters (see Sect. 11.5).

A full hierarchy of approximations based on the quantal fixed-center treat-

ment (20) has been constructed for Rydberg collisions, of which only a few will be outlined next.[9]

11.2c. Born, Coulomb fixed-center, and impulse treatments

Born treatment

In the limit of zero V in (20c), χ_i^+ tends to a plane-wave $\exp(i\mathbf{k}_i\cdot\mathbf{R})$ and (20a) reduces, for inelastic transitions, to the Born approximation written as

$$T_{fi}^{(\mathrm{B})}(\mathbf{K}) = F_{fi}(\mathbf{K})\,T_{\mathrm{el}}^{(\mathrm{B})}(\mathbf{K}), \qquad \mathbf{K} = \mathbf{k}_i - \mathbf{k}_f \tag{22}$$

which is a product of the Born T-matrix element

$$T_{\mathrm{el}}^{(\mathrm{B})}(\mathbf{K}) = \int V_{13}(\mathbf{r}_{13})\exp(i\mathbf{K}\cdot\mathbf{r}_{13})\,d\mathbf{r}_{13} \tag{23}$$

for potential scattering by V_{13} and of

$$F_{fi}(\mathbf{K}) = \langle\phi_f(\mathbf{r})|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi_i(\mathbf{r})\rangle \tag{24}$$

the inelastic form factor for $i\to f$ transitions in the Rydberg atom A. This product (22) is written to emphasize the underlying role in inelastic collisions of elastic collisions, characterized by $T_{\mathrm{el}}^{(\mathrm{B})}$, between the projectile and the Rydberg electron. It can also be recast in the usual and less revealing way as

$$\begin{aligned} T_{fi}^{(\mathrm{B})} &= \langle\phi_f(\mathbf{r})\exp(i\mathbf{k}_f\cdot\mathbf{R})|V(\mathbf{r},\mathbf{R})|\phi_i(\mathbf{r})\exp(i\mathbf{k}_i\cdot\mathbf{R})\rangle \\ &\equiv \int V_{fi}(\mathbf{R})\exp(i\mathbf{K}\cdot\mathbf{R})\,d\mathbf{R} \end{aligned} \tag{25}$$

which is simply the Fourier transform of the coupling interaction (7). The Born integral cross section for $\mathbf{n}(nlm)\to\mathbf{n}'(n'l'm')$ collisional transitions at impact energy E is therefore

$$\sigma_{\mathbf{n},\mathbf{n}'}^{(\mathrm{B})}(E) = \frac{1}{8\pi k_f^2}\left(\frac{2M_{\mathrm{AB}}}{\hbar^2}\right)^2\int_{(k_i-k_f)}^{(k_i+k_f)}|F_{\mathbf{n},\mathbf{n}'}(K)|^2|T_{\mathrm{el}}^{(\mathrm{B})}(K)|^2K\,dK \tag{26}$$

where M_{AB} is the reduced mass of the A–B(n) collision system. For e–B(n) collisions, $T_{\mathrm{el}}^{(\mathrm{B})}$ in (26) is $4\pi e^2/K^2$, which, because of its singularity as $K\to 0$, exerts a dramatic influence on F_{fi} only in the "optical" limit of vanishing K when it effectively amplifies any dipole term in F_{fi}. This dipole then dominates the remaining multipoles at high E with the result that the cross section $\sigma_{\mathbf{nn}'}$ tends to the Bethe asymptotic limit with its characteristic $f_{\mathbf{nn}'}\ln E/E$ dependence in terms of the oscillator strength $f_{\mathbf{nn}'}$ for $\mathbf{n}\to\mathbf{n}'$ transitions. With increasing n and n', however, the onset of this limit is pushed further into regions of much higher E (relative to the location of the cross-sectional peak) such that, for a wide range of E (up to 1000 eV for $2\to 3$ transitions in e–He($2\,^3$S) collisions), the $l\to l\pm 1$ dipole transitions are no longer dominant.[8,19,20]

For H(1s) projectiles remaining in the ground state,

$$T_{el}^{(B)}(K) = \frac{4\pi e^2}{K^2}[1 - F_{1s1s}^2(K)] = \frac{4\pi e^2}{K^2}\frac{K^2(8+K^2)}{(4+K^2)^2} \tag{27}$$

is nonsingular as $K \to 0$ such that the corresponding $\sigma_{\mathbf{nn}'}$ will correlate more closely than e-atom collisions with any systematic trends (Sect. 11.2d) exhibited in $F_{\mathbf{nn}'}$ as $\mathbf{n}$ and $\mathbf{n}'$ are varied.

Coulomb fixed-center treatment

When (21) is a sum of Coulomb interactions

$$V = -(Ze^2/r_{13}) + (ZZ_c e^2/R) \tag{28}$$

as for particles of charge Ze incident on $B(n)$ of core charge $Z_c e$, Flannery[9] provided the exact solution $\Lambda(\lambda)M(\mu)\exp(im\Phi)$ for χ_i^+ in (20c), in terms of prolate-spheroidal coordinates (λ, μ, Φ) such that (20a) is then given by

$$T_{fi} = \langle \phi_f(\mathbf{r})\exp(i\mathbf{k}_f\cdot\mathbf{R})\left|\frac{Ze^2}{R} - \frac{Ze^2}{|\mathbf{R}-\mathbf{r}|}\right|\phi_i(\mathbf{r})\,T_{\mathbf{r}}\Lambda(\lambda\,|\,\mathbf{r})M(\mu\,|\,\mathbf{r})\exp(im\Phi)\rangle \tag{29}$$

where $T_{\mathbf{r}}$ denotes a rotation operator that transforms χ_i from a coordinate axis in which $\mathbf{r}$ is fixed to a space-fixed frame. To zero order, this solution χ_i^+ tends to the unperturbed product of Coulomb functions centered about each scattering center, respectively. Then, by following an analysis similar to that of Vainshtein et al.,[21] the cross section reduces to

$$\sigma_{nn'}(E) = (8\pi/k_i^2 a_0^2)(M_{AB}/m_e)^2 \int_{(k_n - k_{n'})}^{(k_n + k_{n'})} |F_{\mathbf{nn}'}(\mathbf{K})|^2 [f(\nu,\chi)]^2 dK/K^3 \tag{30a}$$

where m_e is the electronic mass. Eq. (30a) is identical with the plane-wave Born approximation (26) except for introduction of

$$f(\nu,\chi) = (\pi\nu/\sinh\pi\nu)F(-i\nu, i\nu, 1, \chi) \tag{30b}$$

where F is a hypergeometric function with arguments

$$\chi = (2\epsilon_{n'n} + K^2)/(2\epsilon_{n'n} + 3K^2), \qquad \nu = k_n^{-1} \text{ or } [k_n + (2\epsilon_n)^{1/2}]^{-1} \tag{30c}$$

in which $\epsilon_{n'n}$ is $(\epsilon_{n'} - \epsilon_n)$, the transition energy in atomic units, and the second value of ν is so designed as to account for the fact that the Rydberg electron is bound to give an effective-charge effect. The result, Eq. (30), derived originally from a first-order treatment[21] replaces the (zero-order) plane-wave $\exp(i\mathbf{k}_i\cdot\mathbf{R})$ for relative motion of the charged projectile in the Born approximation (25) by a product of Coulomb functions that represent the unperturbed relative motion in the field of the fixed Rydberg e and its core. The overall treatment, Eq. (29), of Flannery,[9] which tends to (30) in the first-order limit, is termed the *Coulomb fixed-center approximation* to remind us of the

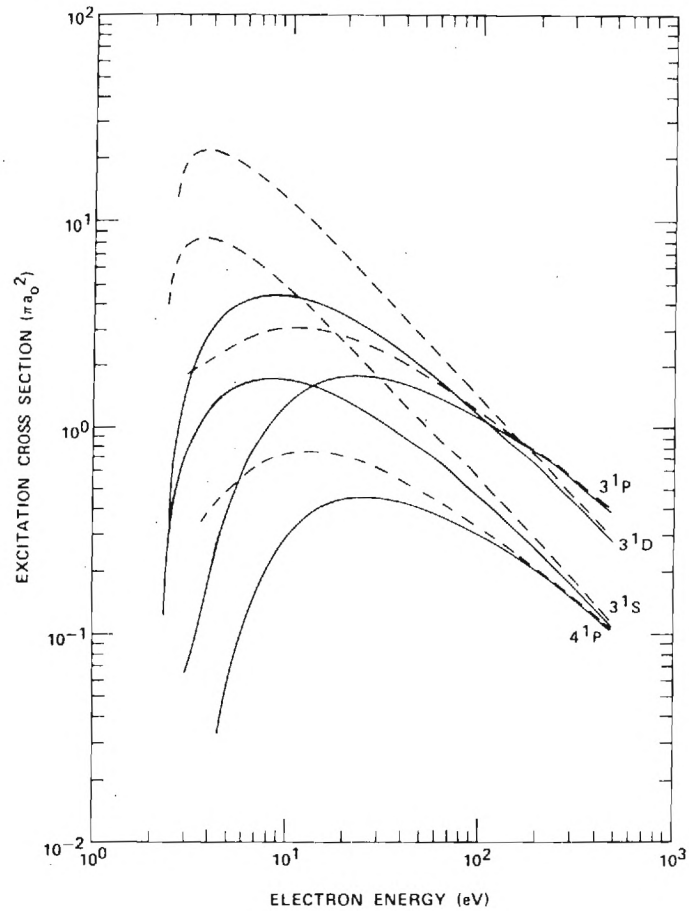

Fig. 11.1. Cross sections (πa_0^2) for the $3\,^1S$, $3\,^1P$, $3\,^1D$, and $4\,^1P$ excitations in e-He($2\,^1S$) collisions. (From Flannery et al.[19]) Broken curves: Born approximation; solid curves: equation (30) generalized to include electron exchange and effective charge. (From Flannery et al.[19])

underlying assumptions and provides systematic improvement to the first-order result of Vainshtein et al.[21]

In charged-particle–Rydberg collisions, the fixed-center treatment is based on the fact that the incident particle is subjected not to the averaged field of the Rydberg electron and its core – the basis of close-coupling perturbation treatments of Sect. 11.2a – but actually to two strong Coulomb-type fields that reduce to the averaged field only for distant encounters.

Flannery et al.[19] investigated (26) and (30) for $2\,^{1,3}S$–$n\,^{1,3}L$ transitions in e-He($2\,^{1,3}S$) collisions through the use of highly accurate wave functions for He. Representative cross sections based on generalization of (30a) to include

electron exchange are displayed in Fig. 11.1. The main feature is that the optically forbidden $2\,^1S \rightarrow 3\,^1D$ transition, and $2\,^1S \rightarrow 3\,^1S$ to a lesser extent, is greater than the $2\,^1S$–$3\,^1P$ optically allowed transition over a large E range. This feature is but an example of a more systematic trend exhibited in collisional transitions between excited states in general.[20] Because of its slower $E^{-1} \ln E$ asymptotic dependence, the optically allowed transition will eventually dominate.

Impulse approximation treatment

When interaction V_{C3} between the core C and projectile A is neglected and the Rydberg wave function $\phi_i(\mathbf{r}_1)$ in (20) is expressed in terms of its momentum wave function or amplitude $g_i(\mathbf{k}_1)$ associated with the Rydberg electron of momentum $\mathbf{k}_1$ by

$$\phi_i(\mathbf{r}_1) = (2\pi)^{-3/2} \int g_i(\mathbf{k}_1) \exp(i\mathbf{k}_1 \cdot \mathbf{r}_1)\, d\mathbf{k}_1 \tag{31}$$

it can be shown[22] that the T matrix (20a) for inelastic scattering of projectile 3 from wave vector $\mathbf{k}_3$ to $\mathbf{k}_3'$ relative to the target core reduces after some analysis to

$$T_{fi}^1(\mathbf{k}_3, \mathbf{k}_3') = \int g_f^*(\mathbf{k}_1') g_i(\mathbf{k}_1)\, T_{13}(\mathbf{k}, \mathbf{k}')\, d\mathbf{k}_1 \{\delta[\mathbf{P} - (\mathbf{k}_1' - \mathbf{k}_1)]\, d\mathbf{k}_1'\} \tag{32a}$$

where

$$T_{13}(\mathbf{k}, \mathbf{k}') = \langle \exp(i\mathbf{k}' \cdot \mathbf{r}) | V_{13}(\mathbf{r}) | \psi(\mathbf{k}, \mathbf{r}) \rangle \tag{32b}$$

is the exact T matrix and ψ is the exact wave function for potential scattering by V_{13} in the (1–3) center of mass such that $\chi_i^+(\mathbf{r}_1, \mathbf{r}_3)$ in (20c) is $\exp(i\mathbf{K}_0 \cdot \mathbf{R}) \times \exp(-i\mathbf{k}_1 \cdot \mathbf{r}_1)\psi(\mathbf{k}, \mathbf{r})$. The δ function in (32a) implies conservation of total linear momentum $\mathbf{K}_0 = (\mathbf{k}_1 + \mathbf{k}_3)$ before and after the (1–3) collision, which changes the momentum of particle i of mass M_i from $\mathbf{k}_i$ to $\mathbf{k}_i'$ such that the momentum change is

$$\mathbf{P} = \mathbf{k}_3 - \mathbf{k}_3' = \mathbf{k}_1' - \mathbf{k}_1 = \mathbf{k}' - \mathbf{k} \tag{32c}$$

where

$$\mathbf{k}^{(\prime)} = \frac{M_3}{M}\, \mathbf{k}_1^{(\prime)} - \frac{M_1}{M}\, \mathbf{k}_3^{(\prime)}, \qquad M = M_1 + M_3 \tag{32d}$$

is the initial (unprimed) or final (primed) momentum of (1–3) relative motion. Expressions (32) represent the quantal impulse approximation (QIA), which can be derived from many different directions.[23] Although the present method of derivation has exposed several underlying assumptions in QIA, the improvement and establishment of rigorous validity criteria are best achieved from the exact two-potential expression, a procedure natural for Rydberg collisions (Sect. 11.5).[2]

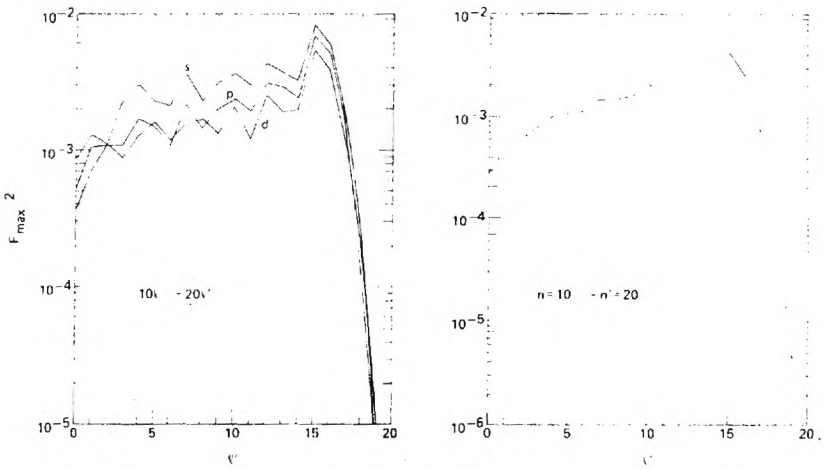

Fig. 11.2. Variation with final angular momentum l' of the peak of the inelastic form factor, Eq. (24), unaveraged and averaged over l for $10l \rightarrow 20l'$ transitions. (From Flannery and McCann[20])

11.2d. Systematic trends in inelastic form factors for $nl \rightarrow n'l'$ collisional transitions

Many sets of quantal Born and related calculations of cross sections for $[e, H^+, H(1s)]$-$H(nl)$ collisions exist (see, for example, Table V of Percival and Richards[12] for partial list and Refs. 24–26 for some additional work). However, by analogy with transitions from ground states, it is tempting to suggest that dipole transitions $nl \rightarrow n'(l \pm 1)$ dominate the remaining multipole collisional transitions between any two excited levels (n, n') and thereby to restrict calculation to only a few transitions with $\Delta l = |l' - l| = 0, 1, 2$, and 3, as in the case of the applications just referenced. As Fig. 11.1 suggests and as Flannery and McCann[20] explicitly showed, this analogy is quite restrictive and is without foundation for $n \rightarrow n'$ transitions in general.

Not only is the inelastic form factor F_{fi} [Eq. (24)] basic to Born's approximation and derivatives, but it is also key to more elaborate efforts such as the impulse, fixed-center, and close-coupling treatments. Because any systematic behavior of F_{fi} with variation in quantum numbers (nlm) is, in general, reflected in Born[20] and more elaborate cross sections and because the maximum in $\sigma^{(B)}_{n,n'}(E)$ originates in (26) from K integration over the largest peak F_{max} in $F_{fi}(K)$, we may initially consider the variation of F_{max} with respect to the initial and final quantum numbers.

$nl \rightarrow n'l'$ Transitions $(n' \gg n)$

Figure 11.2 shows that F_{max} for various l oscillate on an increasing background as l' is increased until a unique value of l'_{max} is attained, after which they

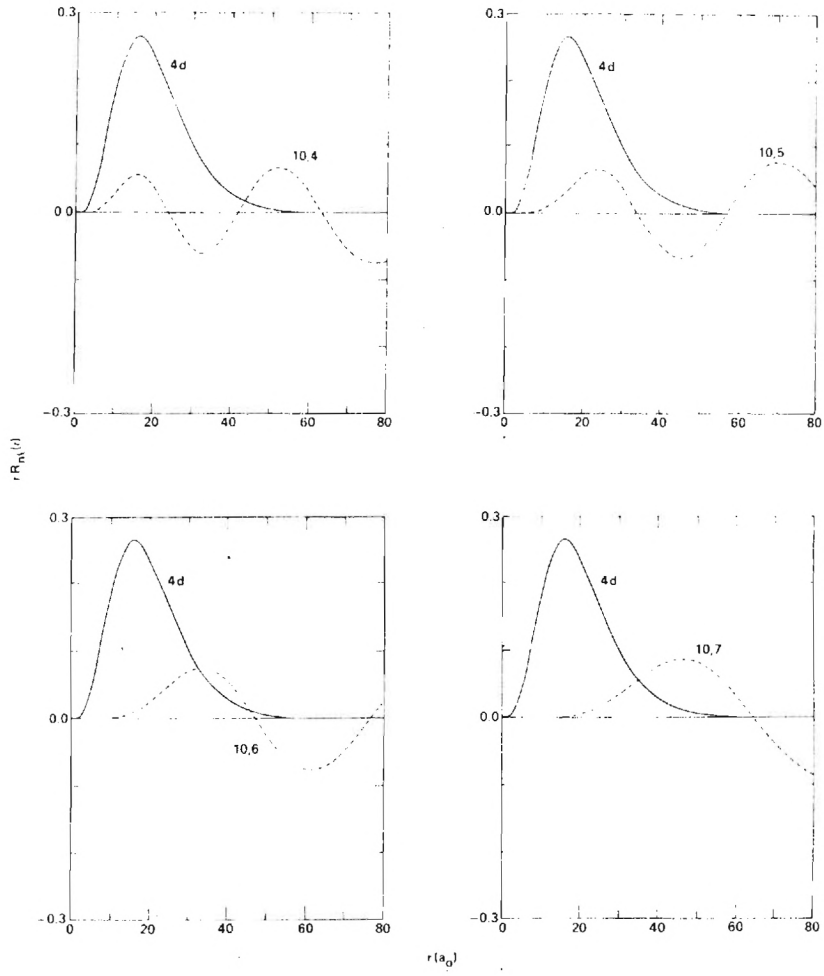

Fig. 11.3. The 4d and $10(l'=4\text{–}7)$ hydrogen radial orbitals R_{nl} times r. Note the outward shift in the $10l'$ orbital and the consequent variation in overlap with increase of l'. Here maximum overlap is obtained for $l'=l'_{\max}=6$.

exhibit a rapid monotonic decrease. The value $l'_{\max}$ is strongly dependent on the initial value of the principal quantum number n, is relatively insensitive to changes in the initial angular momentum quantum number l, and is given by[20]

$$l'_{\max} = \min\left\{(n'-1), \sim\left[n\left(\frac{2(n+3)}{(n+1)}\right)^{1/2} - \frac{1}{2}\right]\right\} \tag{33}$$

The chief contribution to the population of the final level n' in electron-atom and atom-atom collisions arises from the $n[l=0,1,\ldots,(n-1)] \rightarrow n'l'_{\max}$ array of transitions. This array may include some with dipole character, i.e., $l=l'_{\max}\pm 1$; and these dipole transitions tend to be somewhat more probable.

However, the important feature is that l'_{max} is primarily n dependent and, as such, may have a value inaccessible to dipole transitions. For example, the strongest collisional transitions in the $10l \rightarrow 20l'$ array (with variation of l and l') are the set $10l \rightarrow 20(l'_{max} \simeq 15)$, none of which possess dipole character. Because $n' \gg n \gg 1$, the magnitude and range of the initial and final orbits are quite different, as shown in Fig. 11.3 for $(4 \rightarrow 10)$ transitions (because of the relatively large energy separation between the levels), and the expression (33) for l'_{max} is determined[20] from a consideration of the overlap of the initial radial orbital with the first lobe of the final orbital, the region yielding any significant overlap.

The dramatic drop in F_{max} for $l > l'_{max}$ will not be evident unless the final n' is sufficiently large to accommodate that unique l'_{max} fixed by n. The final decline becomes more emphasized by making n' as large as in Fig. 11.2. By averaging over l before varying K and l', the oscillations can be suppressed and the key issues - the rise, the peak, and the rapid decline - become more marked. These trends are preserved in the Born cross sections for transitions in Rydberg atoms induced by e and H(1s) impact (see Ref. 20 for examples for many different $(n \rightarrow n')$ sets of transitions) and also in the more elaborate close-coupling eikonal treatment of even e-He($2\,^{1,3}S$) collisions.[8]

$n \rightarrow n+1$ Transitions

For $n \rightarrow n+1$ transitions, the radial orbitals are almost similar in both magnitude and range (in contrast to that in Fig. 11.3 for $n' \gg n$). Maximum overlap is obtained when all the *innermost* lobes are in phase and almost coincide and each outermost lobe is out of place, as happens when $l \simeq l'$. As l' is increased, the lobe of the final n' orbital moves inward with increasing phase difference between the orbitals. Maximum overlap is again attained when the *outermost* oscillations of both n and n' orbitals are almost out of phase by π or in phase as for the overlap of $n'=11$, $l'=6,7$ with 10s, respectively.[20] With further increase of l', the number of oscillations in the n' orbitals reduces and cancellation occurs, thereby yielding small overlap with the initial state. Low initial l is therefore characterized by two well-separated peaks, one at $l' \simeq l$ and the other at higher l'. As l is increased, these two peaks merge and yield relatively larger form factors and cross sections (see Ref. 20 for detailed examples).

The main conclusions here are that dipole transitions do not, in general, provide the main contribution to $n \rightarrow n'$ collisional transitions unless the initial value of l is $\sim (l_{max} \pm 1)$ and that accurate cross sections require at least evaluation of the full array $nl \rightarrow n'l'_{max}$ of collisional transitions.

11.3. Semiclassical theory of Rydberg collisions

Semiclassical collision treatments in general focus on the transition amplitude $a_{nn'}(\mathbf{R})$ as a function of the relative external vector $\mathbf{R}$, whereas quantal treatments concentrate on scattering amplitudes or eigenphases associated with

each partial wave of total angular momentum of the complete collision system. This feature can be exploited in Rydberg collisions for which $a_{nn'}$ can be exactly determined for transitions involving a large number of equally spaced levels. Semiclassical methods, properly constructed, are based on a stationary-state treatment of the collision process and furnish the scattering amplitude $f_{nn'}(\theta)$ as an $\mathbf{R}$ integral over $a_{nn'}(\mathbf{R})$, or functions thereof, modulated by a Bessel function (Sect. 11.3a). For heavy-particle collisions, a finite number of classical trajectories $R_i(\theta)$ provide the dominant contribution to $f_{nn'}$, which then reduces to $a_{nn'}(R_i(\theta))$ times the amplitude for classical elastic scattering (Sect. 11.3a). In the heavy-particle–high-energy limit, when the scattering is mainly in the forward direction, the integral cross section reduces to the transition probability $|a_{nn'}|^2$ integrated over $2\pi\rho\, d\rho$, where ρ is the impact parameter. Here, the amplitudes $a_{nn'}$ satisfy equations identical to the time-dependent set in Dirac's method of variation of constants for the response of a system to a time-dependent perturbation (Sect. 11.3a).[27] The "time-dependent" semiclassical method (Sect. 11.3b) is therefore valid only in the heavy-particle–high-energy limit and the full stationary-state description (Sect. 11.3a) extends the validity of the semiclassical treatment down to much lower impact energies.

11.3a. Stationary-state treatment

The function F_n for relative motion in (4) is decomposed as

$$F_n(\mathbf{R}) = A_n(\mathbf{R}) \exp[iS_n(\mathbf{R}) - \chi_n(\mathbf{R})] \tag{34}$$

where S_n is real and is identified with the eikonal for relative motion under the static interaction $V_{nn}(\mathbf{R})$ so that

$$S_n(\mathbf{R}) = \int_{\mathbf{R}_0}^{\mathbf{R}} \mathbf{K}_n \cdot d\mathbf{R} + \mathbf{k}_n \cdot \mathbf{R}_0 \tag{35}$$

is the solution of the Hamilton–Jacobi equation,[15] where $\mathbf{R}_0$ is the initial point on the trajectory $\mathbf{R}_n$ at which $K_n = k_n$. When the $\mathbf{R}$ variation in F_n is mainly controlled by S_n, then various second-order terms $\nabla^2(A_f, \chi_f)$, $(\nabla\chi_f)$, and $(\nabla A_f \cdot \nabla\chi_f)$ can be neglected, so that the substitution of (34) into (5) yields the first-order differential equations in three dimensional space:[8, 18]

$$i\mathbf{K}_f \cdot \nabla_{\mathbf{R}} A_f(\mathbf{R}) = \left(\frac{\mu}{\hbar^2}\right) \sum_{n \neq f} A_n(\mathbf{R}) V_{fn}(\mathbf{R}) \exp[i(S_n - S_f)] \exp[-(\chi_n - \chi_f)] \tag{36}$$

where χ_n satisfies

$$\nabla_{\mathbf{R}}^2 S_n - 2(\nabla_{\mathbf{R}} S_n) \cdot (\nabla_{\mathbf{R}} \chi_n) = 0 \tag{37}$$

When S_n and χ_n are purely real, then, for unit A_n, Eq. (34) describes motion of a classical ensemble of particles with momentum ∇S_n and flux density $\exp(-2\chi_n)$. The classical current J_n (number of particles per unit area

per second) in this "elastic" channel n is therefore $\exp(-2\chi_n)|\nabla S_n|/\mu$ such that (37) is equivalent to current conservation $(\nabla \cdot \mathbf{J}_n)=0$ in channel n. With the initial $\mathbf{k}_n$ motion directed along the Z axis with impact parameter $\boldsymbol{\rho}(\rho, \phi)$, then $\chi_n(\mathbf{R}_0)$ is, from (34) and (35), identically zero and the scattered flux across an elemental area $d\mathbf{S}$ normal to the direction $\mathbf{R}(R, \theta, \phi)$ of the outgoing "elastic" scattered wave is, therefore,

$$\lim_{R\to\infty} \{\mu^{-1} \exp[-2\chi_n(\mathbf{R})]\mathbf{K}_n \cdot d\mathbf{S}\} = \mu^{-1}\mathbf{k}_n \cdot d\boldsymbol{\rho} \tag{38}$$

such that $\exp(-2\chi_n)$ as $R \to \infty$ is $[\partial(\tau_n)/\partial(\tau_{n0})]$, where τ_n is the infinitesimal volume along a classical path that evolved from τ_{n0}. Flux is, therefore, lost only by transitions with probability controlled by A_f.

Multichannel eikonal treatment

For collisions of electrons and heavy particles with Rydberg atoms, scattering is mainly in the forward direction (because of the very large internal dipole associated with atoms in a state n high enough for large effective dipole yet low enough so that the Rydberg electron and core do not behave as separate scatterers). The trajectories in (35) and (36) can be assumed identical $(\chi_n - \chi_f \simeq 0)$ and rectilinear $(\chi_n \simeq 0)$ along the initial Z direction so that the matrix element for direct $i \to f$ transitions is

$$T_{fi}(\mathbf{k}_f, \mathbf{k}_i) = \langle \phi_f(\mathbf{r}) \exp(i\mathbf{k}_f \cdot \mathbf{R}) | V(\mathbf{r}, \mathbf{R}) | \sum_n A_n(\mathbf{R})\phi_n(\mathbf{r}) \exp iS_n(\mathbf{R}) \rangle \tag{39}$$

where the transition amplitudes are solutions of

$$iK_f \, \partial A_f(\mathbf{R})/\partial Z = (\mu/\hbar^2) \sum_n A_n(\mathbf{R}) V_{fn}(\mathbf{R}) \exp i(S_n - S_f) \tag{40}$$

These equations represent the multichannel eikonal treatment of Flannery and McCann,[8] which was developed more formally via linearization of the Green's function propagator (see last listing in Ref. 8). The method proved to be very reliable for both heavy-particle collisions[28] at energies where forward scattering predominates and for electron–(ground-state) atom inelastic scattering[8] by $\theta \lesssim 40°$ at impact energies E greater than a few times the ionization threshold. Its application to e–He($2^{1,3}$S) collisions represents, as yet, the only direct application of any stationary-state closely coupled procedure to e-excited atom collisions (see last listing in Ref. 8). It is applicable to detailed collisional transitions $(nl \to n'l')$, particularly between close levels $n \simeq n'$, by electron, ion, and neutral impact. The matrix elements V_{fn} can be determined from correspondence principles (Sect. 11.4).

Development of (39) and (40) follows by setting

$$a_f^{(E)}(\boldsymbol{\rho}, Z) = A_f(\boldsymbol{\rho}, Z) \exp\left[i \int_{-\infty}^{Z} (K_f - k_f)\, dZ\right] \exp[i\,\Delta\Phi] \tag{41}$$

where $\mathbf{R}(R,\theta,\Phi)\equiv\mathbf{R}(\rho,\Phi)$, where Δ is the change (m_f-m_i) in the magnetic quantum number of the Rydberg atom, and $a_f^{(E)}(\rho,-\infty)=\delta_{fi}$ ensures that the system wave function $\Psi\simeq\phi_i(\mathbf{r})\exp(ik_iZ)$ as $Z\to-\infty$. Hence (40) reduces to the set

$$i\frac{\hbar^2}{\mu}K_f\frac{\partial a_f^{(E)}}{\partial Z}+\left[\frac{\hbar^2}{\mu}K_f(K_f-k_f)+V_{ff}\right]a_f^{(E)}$$
$$=\sum_{n=1}^{N}a_n^{(E)}(\rho,Z)V_{fn}(\rho,Z)\exp i(k_n-k_f)Z \tag{42}$$

The scattering amplitude on Φ-integration in (39) becomes[8]

$$f_{if}^{\mathrm{ME}}(\theta,\phi)=-i^{\Delta+1}\int_0^\infty J_\Delta(K'\rho)[I_1(\rho,\theta)-iI_2(\rho,\theta)]\rho\,d\rho \tag{43}$$

where K' is the momentum increase $k_f\sin\theta$ in the direction $\hat{\rho}$, J_Δ the Bessel functions of integral order, and

$$I_1(\rho,\theta;\alpha)=\int_{-\infty}^{\infty}K_f\left(\frac{\partial a_f^{(E)}}{\partial Z}\right)\exp(i\alpha Z)\,dZ,\qquad\alpha=k_f(1-\cos\theta) \tag{44}$$

is the main contributor because

$$I_2(\rho,\theta;\alpha)=\int_{-\infty}^{\infty}[K_f(K_f-k_f)+(\mu/\hbar^2)V_{ff}]a_f^{(E)}\exp(i\alpha Z)\,dZ \tag{45}$$

contributes only at lower impact energies.

Equations (42)–(45) represent the full multichannel eikonal (ME) treatment.[8] Approximation follows when

$$K_f\simeq k_f-(\mu/\hbar^2k_f)V_{ff}(\mathbf{R})\qquad\text{for}\quad k_f^2\gg(2\mu/\hbar^2)V_{ff} \tag{46}$$

such that I_2 and the second term on the left-hand side of (42) vanish. For higher energies $K_n\simeq k_n$, in the high-energy–heavy-particle limit of relative speed v_i,

$$k_f=k_i-(\epsilon_{fi}/\hbar v_i)[1+(\epsilon_{fi}/2\mu v_i^2)+\cdots] \tag{47}$$

such that (43) reduces to

$$f_{if}^{(1)}(\theta,\phi)=-i^{\Delta+1}k_i\int_0^\infty\rho\,d\rho\,J_\Delta(K'\rho)\left[\int_{-\infty}^{\infty}(\partial a_f/\partial Z)\exp(i\alpha' Z)\,dZ\right] \tag{48}$$

where $\alpha'=(k_i-k_f)-(\epsilon_{fi}/\hbar v_i)$ and the amplitudes a_f satisfy

$$i\hbar\frac{\partial a_f}{\partial t}=\sum_{n=1}^{N}a_f(\rho,Z)V_{fn}(\rho,Z)\exp(i\omega_{fn}t);\qquad\hbar\omega_{fn}=\epsilon_{fn} \tag{49}$$

in which the dummy variable t in $Z=v_it$ specifies variation along the straight-line path. When α' can be neglected, as in the high-energy limit, then (48) reduces to

$$f_{if}^{(2)}(\theta, \phi) = -i^{\Delta+1} k_i \int_0^\infty J_\Delta(K'\rho)[a_f(\rho, \infty) - \delta_{if}]\rho \, d\rho \tag{50}$$

In the sudden approximation [i.e., when the collision time $\tau_{\text{coll}} \ll 2\pi/\omega_{fi} \simeq T/(f-i)$, where the classical period T of the orbital Rydberg electron has been introduced by Bohr's correspondence (Sect. 11.4a)], then set (49) can be solved exactly to give

$$a_f^{(s)}(\rho, Z) = \left\langle \phi_f(\mathbf{r}) \middle| \exp\left[-(i/\hbar)\int_{-\infty}^{t} V(\mathbf{r}, \mathbf{R})\, dt\right] \middle| \phi_i(\mathbf{r}) \right\rangle, \qquad Z = v_i t \tag{51}$$

The Glauber approximation is recovered by substitution of (51) into (50).[8] The differential cross section for $i \to f$ collisional transitions given by the full ME treatment (42)–(45) and by its approximation I [Eqs. (48) and (49)] and II [Eq. (50)] is

$$\sigma_{if}(k_i) = 2\pi(k_f/k_i)\int_0^\pi |f_{if}^{(\text{ME},1)}(\theta, \phi)|^2 \, d(\cos\theta) \tag{52}$$

which reduces for approximation II (50) to

$$\sigma_{if}(k_i) = 2\pi(k_f/k_i)\int_0^\infty |a_f(\rho, \infty) - \delta_{if}|^2 \rho \, d\rho \tag{53}$$

Thus (53) is a valid representation only in the heavy-particle–high-energy limit as previously outlined, whereas (52) extends the validity down to intermediate and lower energies. For example, (52) is accurate for 1s–2p and $1\,^1\text{S}$–$2\,^1\text{P}$ transitions in e–H(1s) and e–He($1\,^1\text{S}$) collisions for impact energies $E \gtrsim 2I$, twice the ionization energies, whereas (53) tends to accurate values only for $E \gtrsim 10I$.[8]

Multistate orbital treatment

We note that the basic expression (39) for a given scattering angle θ provides contributions from all regions of $\mathbf{R}$ space and not just those $\mathbf{R}$ associated with an external classical trajectory $R_n(\theta)$. For heavy-particle collisions at lower energies, when the main contribution to both the phase and magnitude of the scattering amplitude arises from the trajectories $R_n(\theta)$, which are not in the forward direction, then the multistate orbital treatment can be adopted for Rydberg collisions.[18] From (38),

$$\lim_{R\to\infty} \exp[-2\chi_n(\mathbf{R})] = \left(\frac{\partial \tau_{no}}{\partial \tau_n}\right) = \left[\frac{\rho \, d\rho \, d\phi}{R^2 \, d(\cos\theta)\, d\phi}\right] = \frac{1}{R^2}\left(\frac{d\sigma_{\text{CL}}^{(n)}}{d\Omega}\right) \tag{54}$$

where $\sigma_{\text{CL}}^{(n)}$ is the classical cross section for elastic scattering by angle θ under V_{nn} in channel n. The scattered amplitude $f_{ni}(\theta)$ for $i \to n$ transitions then follows from the outgoing spherical wave of (4) with the aid of (54) in (34) to yield

$$f_{ni}(\theta) = \lim_{R\to\infty} A_n(\mathbf{R})\{\exp[-iS_n'(\mathbf{R})]\}[\sigma_{el}^n(\theta)]^{1/2} \tag{55}$$

where S_n' is the classical action along the nth path measured relative to the action along the path of undeflected particles with the same wave number K_n, i.e.,

$$S_n'(R) = -(1/\hbar)\int_{\mathbf{R}_0}^{\mathbf{R}} \mathbf{R}_n \cdot \mathbf{P}_n\, dt; \qquad \mathbf{P}_n \equiv \hbar\mathbf{K}_n \equiv \mu\, d\mathbf{R}_n/dt \tag{56}$$

in terms of the external relative momentum $\mathbf{P}_n$. The amplitudes $A_n(\mathbf{R})$ are solutions of (36), where it proves convenient to write

$$i\mathbf{K}_f \cdot \nabla_{\mathbf{R}} A_f(\mathbf{R}) \equiv i\mathbf{K}_f \cdot \hat{\mathbf{s}}_f\, \partial A_f(\rho, s_f)/\partial s_f = (i\mu/\hbar)\,\partial A_f(\rho, t)/\partial t \tag{57}$$

in terms of $\mathbf{s}_f$ the vector distance traveled along the trajectory $\mathbf{R}_f$ with initial impact parameter ρ and where "time" t is merely a dummy variable invoked only to classify variation along the trajectories specified by $\mathbf{R}_f$. When the momentum $\mathbf{P}$ is the mean $\hbar(\mathbf{K}_n + \mathbf{K}_f)/2$, directed along some averaged trajectory $\mathbf{R}(t)$ common to all channels n, then $\chi_n \simeq \chi_f$ in (36) and the difference $(S_n - S_f)\hbar$ of classical action in channels n and f evolves as

$$S_n(\mathbf{R}) - S_f(\mathbf{R}) = \omega_{fn} t + (1/\hbar)\int_{t_0}^{t} [V_{ff}(\mathbf{R}(t) - V_{nn}(\mathbf{R}(t))]\, dt \tag{58}$$

such that (49) is recovered from (40) via (57) and the transformation $a_f = A_f \exp[-(i/\hbar)\int_{t_0}^{t} V_{ff}\, dt]$. The scattering amplitude (55) is therefore

$$f_{ni}^{(j)}(\theta) = a_n(\rho_j, t\to\infty)\exp\left[\frac{i}{\hbar}\int_{t_0}^{t}\{V_{nn}[\mathbf{R}(t)] + \mathbf{R}\cdot\mathbf{P}(t)\}\, dt\right]\left[\frac{d\sigma_{CL}(\theta)}{d\Omega}\right]^{1/2} \tag{59}$$

where one impact parameter ρ_j yields scattering angle θ (which, in terms of the deflection angle Θ, is $|\Theta \pm 2\pi m|$ for integer m). The differential cross section is simply

$$(d\sigma_{if}/d\Omega) = |a_f(\rho_j, t\to\infty)|^2\,(d\sigma_{CL}/d\Omega) \tag{60}$$

When more than one trajectory j yields a given θ, then interference occurs between the phases associated with each trajectory and a three-dimensional generalization[18] of the usual one-dimensional analysis yields

$$f_{ni}(\theta) = -i\sum_{j=1}^{N} \alpha_j\beta_j f_{ni}^{(j)}, \qquad \alpha_j, \beta_j = \exp(\pm i\pi/4) \tag{61}$$

where the exponent of α_j is positive or negative, depending on whether the scattered particle emerges on the same side of the axis it entered (as in an overall repulsive collision) or on the opposite side (as in an overall attractive collision) and where the exponent of β_j is positive or negative as $d\Theta/d\rho$ is, respectively, positive or negative (see second listing in Ref. 18). When these trajectories coalesce, as for caustics (e.g., a rainbow), representation by classi-

cal trajectories becomes invalid and a (uniform) solution, which tends to (61) for well-separated trajectories, is then obtained in terms of Airy functions.[18]

The orbit common to all channels n is determined by the averaged Hamiltonian[18]

$$\bar{H} = \langle \Psi | H | \Psi \rangle = \sum_{k=1}^{3} (1/2\mu) P_k^2(\mathbf{R}) + \mathcal{V}_{\text{opt}}(\mathbf{R}) \tag{62}$$

where Ψ is defined by (4) with (34) and H by (1). The first term on the right-hand side of (62) is the kinetic energy of relative motion (obtained by assuming that $S_n(\mathbf{R})$ in (34) contains the major $\mathbf{R}$ variation). The second term

$$\mathcal{V}_{\text{opt}}(\mathbf{R}) = \sum_n [|a_n(t)|^2 \epsilon_n + \sum_f a_f^*(t) a_n(t) V_{fn}[\mathbf{R}(t)] \exp(i\omega_{fn} t)] \tag{63}$$

behaves like an optical potential that effectively couples response (4) provided by the transition amplitudes a_f to the interaction $V(\mathbf{r}, \mathbf{R})$ back to the relative motion and vice versa. The common trajectory is then given by the solution of Hamilton's equations of motion:

$$\begin{aligned} \frac{\partial Q_k}{\partial t} &= \frac{\partial \bar{H}}{\partial P_k} \equiv \frac{1}{\mu} P_k(t) \\ \frac{\partial P_k}{\partial t} &= -\frac{\partial \bar{H}}{\partial Q_k} = -\frac{\partial V_{\text{opt}}}{\partial Q_k} = -\sum_n \sum_f a_f^*(t) a_n(t) \frac{\partial V_{fn}(Q_k)}{\partial Q_k} \exp(i\omega_{fn} t) \end{aligned} \tag{64}$$

for the variation with time t of the generalized coordinates $Q_k \equiv (X, Y, Z)$ for $\mathbf{R}$ and their conjugate momenta P_k. The solutions of (64) are therefore coupled to the complex solutions a_f of (49), thereby resulting in $(2N+4)$ coupled equations rather than $2N$ for rectilinear trajectories. This semiclassical procedure reproduces[18] with remarkable accuracy differential and integral collisions, together with detailed oscillatory structure due to interference between the action S_f' phases peculiar to contributing classical paths.

A valuable feature of scattering by $\mathcal{V}_{\text{opt}}$ is that total energy E of the collision system is conserved, which is confirmed by showing, with the aid of (63) and (64), that $(d\bar{H}/dt) = (\partial \bar{H}/\partial t) = 0$.[18]

In this multistate orbital treatment, energy is therefore continually being redistributed between the relative motion and the internal degrees of freedom as motion along the trajectory proceeds, which is a unique and valuable asset, particularly for Rydberg collisions with ions, atoms, and molecules at thermal and higher energies.

When this coupling between internal and external motions is ignored by assuming some averaged spherical interaction $\bar{V}(R)$ independent of transition amplitudes $a_n(t)$, then the time variation of $\mathbf{R}(R, \Theta, \Phi)$ given by (64) is

$$dR/dt = \pm \bar{v}[1 - (\rho^2/R^2) - \bar{V}(R)/E]^{1/2} \qquad d\Theta/dt = \bar{v}\rho/R^2 \tag{65}$$

where $\bar{v}$ is some averaged speed and Φ is a constant.

11.3b. "Time-dependent" treatment: classical path, Magnus, and sudden approximations

Next attention will be focused only on the response of the target system to a time-dependent interaction generated by the passing projectile. Thus (1) is replaced by the time-dependent Schrödinger equation

$$H\Phi = [H_0(\mathbf{r}) + V(\mathbf{R}(t), \mathbf{r})]\Phi(\mathbf{r}, t) = i\hbar\,\partial\Phi(\mathbf{r}, t)/\partial t \tag{66}$$

and the response is expanded as

$$\Phi(\mathbf{r}, t) = \sum_n a_n(t)\phi_n(\mathbf{r}) \exp(-i\omega_n t) \tag{67}$$

where the transition amplitudes are determined by

$$i\hbar\,\partial a_f(t)/\partial t = \sum_n a_n(t) V_{fn}(\mathbf{R}(t)) \exp(i\omega_{fn} t) \tag{68}$$

subject to $a_f(t \to -\infty) = \delta_{ni}$, as given by Dirac's method of variation of constants.[27] Although in this treatment the inelastic integral cross sections are

$$\sigma_{if} = \int_0^\infty |a_f(\boldsymbol{\rho}, \infty)|^2 \, d\rho \tag{69}$$

the treatment provides no details on either integral elastic or differential scattering cross sections without recourse to the preceding stationary-state analysis.

Upon use of a straight-line trajectory

$$\mathbf{R} = \boldsymbol{\rho} + \mathbf{v}t \tag{70}$$

(69) reduces to the standard impact-parameter result. Because (68) is identical to (49) obtained as a high-energy approximation to the basic stationary-state analysis [Eqs. (42)–(45)], the transition amplitudes a_f computed from (68) may be inserted directly into (48) or (50)–(53) for the various scattering amplitudes and cross sections.[8,28] By comparison, we note that (69) with a straight-line path (70) provides a valid representation of the inelastic cross sections *only in the high-energy–heavy-particle collision limit,* which has been used[12,29] for e–H(n) inelastic cross sections that are claimed to be accurate for impact energies $E > 4I_n$, a claim that may be optimistic because (69) for H(1s–2p) collisional excitation becomes accurate only for $E > 10I_1$. Validity to lower energies can be extended through the use of a_f in (50) or, even better, by solution of the full ME equations (42)–(45) for use in (52).

Valuable information on the transition amplitudes for high-Rydberg atoms can be obtained, however, from (68), which becomes considerably simplified through the use of the Bohr and Heisenberg correspondence principles (Sect. 11.4b) such that an exact solution (the equivalent oscillator theorem; Sect. 11.4d) is obtained.

In the preceding Schrödinger picture, the time variation of Φ is developed by the full Hamiltonian (H_0+V) in (66). A complete hierarchy of approximation to (1) becomes more transparent in the interaction picture,[30] where the transformed interaction

$$V_{\mathrm{I}}(t) = \exp\left(\frac{i}{\hbar} H_0 t\right) V(t) \exp\left(-\frac{i}{\hbar} H_0 t\right) \tag{71}$$

controls the full-time evolution of the transformed wave function

$$\Phi_{\mathrm{I}}(\mathbf{r}, t) = \exp\left(\frac{i}{\hbar} H_0 t\right) \Phi(\mathbf{r}, t) \equiv \sum_{p=0}^{\infty} \frac{1}{p!} \left(\frac{i}{\hbar} H_0 t\right)^p \Phi(\mathbf{r}, t) \tag{72}$$

which, with the aid of (66) satisfies,

$$i\hbar\, \partial \Phi_{\mathrm{I}} / \partial t = V_{\mathrm{I}}(\mathbf{r}, t) \Phi_{\mathrm{I}}(\mathbf{r}, t) \tag{73}$$

Thus, in this representation, the free-particle states that remain independent of t are simply $\phi_n(\mathbf{r})$, such that the system wave function in (73) can be expanded as

$$\Phi_{\mathrm{I}}(\mathbf{r}, t) = \sum_n a_n(t) \phi_n(\mathbf{r}) \tag{74}$$

to give, in matrix notation,

$$i\hbar \dot{\mathbf{a}} = \mathbf{V}_{\mathrm{I}}(t) \mathbf{a} \tag{75}$$

where $\mathbf{a} \equiv \{a_n\}$ and the matrix elements of the anti-Hermitian matrix $\mathbf{V}_{\mathrm{I}}$ $(\equiv -\mathbf{V}_{\mathrm{I}}^{\dagger})$ of (71) are

$$(V_{\mathrm{I}})_{mn} = \langle \phi_m(\mathbf{r}) | V_{\mathrm{I}}(\mathbf{r}, t) | \phi_n(\mathbf{r}) \rangle \equiv V_{mn} \exp(i\omega_{mn} t) \tag{76}$$

so that (75) and (68) are equivalent. Then we introduce the operator $\mathbf{U}$, which translates Φ_{I} in time as

$$\Phi_{\mathrm{I}}(t) = \mathbf{U}(t, t_0) \Phi_{\mathrm{I}}(t_0) \tag{77}$$

Because $\mathbf{a}$ provides the full-time development of Φ_{I}, then

$$\mathbf{a}(t) = \mathbf{U}(t, t_0) \mathbf{a}(t_0) \tag{78}$$

The unitary property of $\mathbf{U}$ (i.e., $\mathbf{U}\mathbf{U}^{\dagger} = \mathbf{I}$) ensures conservation of transition probability and $\mathbf{U}(t_0, t_0)$ is the unit operator $\mathbf{I}$. From (75)

$$i\hbar\, d\mathbf{U}(t, t_0)/dt = \mathbf{V}_{\mathrm{I}}(t) \mathbf{U}(t, t_0) \tag{79}$$

which, on integration, yields,

$$\mathbf{U}(t, t_0) = \mathbf{I} - (i/\hbar) \int_{t_0}^{t} \mathbf{V}_{\mathrm{I}}(t_1) \mathbf{U}(t_1, t_0)\, dt_1 \tag{80}$$

such that iteration provides the expansion series

$$\mathbf{U}(t,t_0) = \mathbf{I} - \frac{i}{\hbar}\int_{t_0}^{t} \mathbf{V}_I(t_1)\,dt_1 + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \left[\int_{t_0}^{t_1} \mathbf{V}_I(t_1)\mathbf{V}_I(t_2)\,dt_2\right] + \cdots \tag{81}$$

$$\equiv \tilde{T}\left[\exp\left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} \mathbf{V}_I(t)\,dt\right] \tag{82}$$

The chronological operator $\tilde{T}$ generates in (81) the time ordering that is essential because $\mathbf{V}_I(t_1)$ and $\mathbf{V}_I(t_2)$ in the interaction picture will, in general, not commute for $t_1 \neq t_2$. Although (81), known as the *the Dyson expansion,*[31] is similar in form and in difficulty of calculation to the Born expansion in stationary-state theory, it can be suitably rearranged[32] so that truncation of the resulting series retains the unitarity of $\mathbf{U}$ at each level of approximation. *The Magnus expansion* is therefore written as

$$\mathbf{U}(t,t_0) = \exp \mathbf{A}(t,t_0) = \mathbf{I} + \mathbf{A}(t,t_0) + \frac{1}{2!}\mathbf{A}^2(t,t_0) + \cdots \tag{83}$$

where

$$\mathbf{A} = \sum_{k=1}^{\infty} (i\hbar)^{-k}\mathbf{A}^{(k)}(t,t_0)/k! \tag{84a}$$

of which the first few terms are

$$\mathbf{A}^{(1)}(t,t_0) = \int_{t_0}^{t} \mathbf{V}_I(t_1)\,dt_1 \tag{84b}$$

$$\mathbf{A}^{(2)}(t,t_0) = \int_{t_0}^{t} dt_1 \left\{\int_{t_0}^{t_1} dt_2\,[\mathbf{V}_I(t_1), \mathbf{V}_I(t_2)]\right\} \tag{84c}$$

where $[\mathbf{V}_I(t_1), \mathbf{V}_I(t_2)]$, the commutator of the interaction $\mathbf{V}_I$, is, as $\mathbf{V}_I$, also anti-Hermitian. Thus $\mathbf{U}$ of (83) retains its unitarity [because $(\exp \mathbf{A})^\dagger = \exp(-\mathbf{A})$] in (84b, c) and in all higher terms, as

$$\mathbf{A}^{(3)}(t,t_0) = \int_{t_0}^{t} dt_1 \left\{\int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3\,[[\mathbf{V}_I(t_1), \mathbf{V}_I(t_2)], \mathbf{V}_I(t_3)] + [[\mathbf{V}_I(t_3), \mathbf{V}_I(t_2)], \mathbf{V}_I(t_1)]\right\} \tag{84d}$$

We shall show in Sect. 11.4d that an exact solution (expressed as an equivalent oscillator theorem) to (79) can then be obtained from (83) for high-energy Rydberg collisions upon transformation to an action-angle $(\mathbf{J}, \mathbf{w})$ representation for the unperturbed functions of $H_0(\mathbf{J})$ and the use of the Bohr and Heisenberg correspondences such that $\mathbf{V}_I(t)$ then commutes at all times.

In the full quantal theory (Sect. 11.2a), the transition probability is given by quantal matrix elements as

$$P_{fi}^{(Q)} = |S_{fi}^{(Q)}|^2 = |\langle \Psi_f^- \mid \Psi_i^+ \rangle|^2$$
$$= |\langle \phi_f(\mathbf{r}) \exp(i\mathbf{k}_f \cdot \mathbf{R}) | S^{(Q)} - 1 | \phi_i(\mathbf{r}) \exp(i\mathbf{k}_i \cdot \mathbf{R}) \rangle_{\mathbf{r},\mathbf{R}}|^2 \quad (85)$$

where $\Psi_i^{\pm}$ are the appropriate solutions, with outgoing (+) and incoming (−) scattered waves, of the stationary-state wave equation (1) and where $S_{fi}^{(Q)}$ are elements of the scattering matrix $\mathbf{S}^{(Q)}$ associated with the quantal scattering operator $S^{(Q)}$. The corresponding probability in the "time-dependent" semiclassical formulation is

$$P_{fi}^{(SC)}(t) = |\langle \phi_f | \Phi_I(t) \rangle|^2 = |\langle \phi_f | U(t, -\infty) | \phi_i \rangle|^2 \quad (86)$$

so that, by analogy with (85), a time-dependent semiclassical scattering operator can be defined as

$$\bar{S}^{(SCH)}(t) = U(t, -\infty) + 1 \quad (87)$$

with matrix elements $\bar{S}_{fi}^{(SCH)}$ given simply by the transition amplitude $a_{fi}(t)$ where the added subscript i denotes solution of (68) appropriate to $a_{fi}(t \to -\infty) = \delta_{fi}$. Note that $\bar{S}_{fi}^{(SCH)}$ is only a heavy-particle–high-energy approximation to the actual quantal $\mathbf{S}_{fi}^{(Q)}$ scattering matrix. True semiclassical time-independent scattering matrix elements $S_{fi}^{(SC)}$ are defined via the multichannel eikonal treatment (Sect. 11.3a) by

$$|\langle \phi_f(\mathbf{r}) \exp(i\mathbf{k}_f \cdot \mathbf{R}) | S^{(SC)} - 1 | \phi_i(\mathbf{r}) \exp(i\mathbf{k}_i \cdot \mathbf{R}) \rangle|^2 = -2\pi i \delta(E_i - E_f) T_{fi}$$
$$= (i\hbar/\mu) f_{if}^{(ME)}(\mathbf{k}_i, \mathbf{k}_f) \quad (88)$$

where $f_{if}^{(ME)}$ is given by (43), which tends, in the high-energy limit, to (50). This distinction between the true semiclassical $S^{(SC)}$ scattering operator and its high-energy limit $\bar{S}^{(SCH)}$ is important. A bar as in $\bar{S}$ is used to denote this distinction.

Because each component matrix $\mathbf{A}^{(k)}$ in (84a) remains anti-Hermitian, the semiclassical transition probability $\mathbf{a}(t)\mathbf{a}^{\dagger}(t)$ is conserved at all times. When $\mathbf{V}_I(t)$ commutes at all times, an exact solution from (84) to (79) is

$$\bar{\mathbf{S}}^{(1)} = \exp\left[-(i/\hbar) \int_{-\infty}^{t} \mathbf{V}_I \, dt \right] \quad (89)$$

Because

$$e^{\mathrm{A}} \mathrm{B} e^{-\mathrm{A}} \equiv e^{[\mathrm{A}\cdot]} \mathrm{B}$$
$$= \mathrm{B} + [\mathrm{A}, \mathrm{B}] + \frac{1}{2!}[\mathrm{A}, [\mathrm{A}, \mathrm{B}]] + \frac{1}{3!}[\mathrm{A}, [\mathrm{A}, [\mathrm{A}, \mathrm{B}]]] + \cdots \quad (90)$$

where the commutator operator $[\mathrm{A}\cdot]$ simply produces the commutator, then

$$V_I = e^{(i/\hbar)H_0 t} V e^{-(i/\hbar)H_0 t}$$

$$= V + \left(\frac{it}{\hbar}\right)[H_0, V] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2 [H_0, [H_0, V]] + \cdots \tag{91}$$

reduces to the first term V, provided H_0 and V commute, which is also a necessary condition for $V_I(t_1)$ and $V_I(t_2)$ to commute. Hence from (89)

$$\bar{S}_{mn}^{\text{EXACT}} = \left\langle \phi_m \middle| \exp\left[-(i/\hbar)\int_{-\infty}^{t} V\,dt\right] \middle| \phi_n \right\rangle, \qquad [H_0, V] = 0 \tag{92}$$

is exact, provided H_0 and V commute, i.e., when $V_{mn}(\epsilon_m - \epsilon_n)$ vanishes.

Under particular conditions fulfilled in general by Rydberg atoms, $[H_0, V]$ is zero, so that (92) is then the exact scattering matrix at *high impact energies*. This circumstance is also fulfilled in general when $(\omega_{fn} t)$ in (76) is effectively zero, i.e., when the collision time $\tau_{\text{coll}} \ll 2\pi/\omega_{mn} \simeq T/(m-n)$, where T is the orbital classical internal period. Equation (92) is the *sudden approximation*. When inserted for a_m in (50) and (51), (92) yields

$$f_{mn} = -\frac{ik_m}{2\pi}\int e^{i\mathbf{K}\cdot\boldsymbol{\rho}} S_{mn}(\boldsymbol{\rho}, t \to \infty)\,d\boldsymbol{\rho} \tag{93}$$

for the scattering amplitude which reduces, with the aid of the straight-line trajectory (70) to the Glauber approximation.[8]

When H_0 and V do not commute, then (89) is the solution obtained from (83) to zero order in the commutator $[V_I(t_1), V_I(t_2)]$ and to all powers in V_I alone. Expanding (89) to first order in V_I then yields

$$\bar{S}_{fi}^{\text{B}} = -(i/\hbar)\int_{-\infty}^{t} V_{fi}(\mathbf{R}(t)) \exp(i\omega_{fi} t)\,dt \tag{94}$$

which is known as the "Born impact-parameter" transition amplitude when the straight-line trajectory (70) is appropriate for the external motion but which obviously holds for a general classical trajectory $\mathbf{R}(t)$.

In conclusion, differential and, hence, integral cross sections for electron, ion, and neutral collisions with Rydberg atoms are given by the multichannel eikonal treatment (42)–(45) and (52) when scattering is mainly in the forward direction ($\lesssim 40°$). As the impact energy is increased, the cross sections tend to those calculated from the solutions a_f of (68) inserted in (50) and (52) and in the high-energy–heavy-particle limit to (53).

When scattering into larger angles becomes important, as for thermal-energy ion and atom impacts, then the multistate orbital treatment (59) is valuable, with $\sigma_{\text{CL}}(\theta)$ in (59) based on either the optical potential $\mathcal{V}_{\text{opt}}$ of (63) or on some spherical average $\bar{V}(R)$ as (65).

11.4. Quantal–classical correspondences

11.4a. Bohr–Sommerfeld quantization

As the principal quantum number n of a Rydberg atom is increased, the electron in the highly excited state eventually behaves as a classical particle in the

sense that it is becoming increasingly localized in (p, q) phase space, where the quantal imprecisions Δq_n and Δp_n associated with its generalized coordinates q_n and conjugate momenta p_n are much less than q_n and p_n, respectively. However, quantal characteristics remain evident, as exhibited, for example, by the detection in H I and H II regions of hot stars of radio-frequency line emissions between neighboring levels n (up to ~250 at present). The link between a classical description of the bound electron and the observable quantal properties is provided by the generalized Bohr–Sommerfeld quantization rule,[33] which states that the classical action

$$A_i = J_i \Delta w_i = \oint p_i \, dq_i$$

$$= 2\pi\hbar(n_i + \alpha_i), \qquad n_i = 0, 1, 2, \ldots, \qquad \alpha_i = \begin{cases} 0, & \text{rotation } q_i \\ \frac{1}{2}, & \text{libration } q_i \end{cases} \tag{95}$$

is equal to the quantum h of action times an integer n_i or half-integer $(n_i + \frac{1}{2})$, depending on whether q_i for periodic motion is a rotation or libration variable, respectively. When q_i and p_i have the same frequency, then the orbit in phase space is closed, which yields a motion (radial motion, harmonic oscillator) designated by the astronomical term *libration* and bounded by zeros in the kinetic energy. When p_i is some periodic function of q_i, which, on increase by a fixed period q_0, does not change the configuration of the system, then the phase-space orbit is not closed and the motion is designated as *rotation* (e.g., a rigid rotor). The q_i integration in (95) is over a complete period of oscillation or of rotation of q_i.

When the frequency of the classical periodic motion is highlighted (as in radiation theory), then the motion is more conveniently represented in terms of action-angle variables (J, w) than in terms of the classical trajectory of the particle in (p, q) phase space. Transformation between the two sets of variables (p, q) and (J, w) is achieved via knowledge of a generating function $S(q, J)$, which is such that[15,16]

$$p = \partial S(q, J)/\partial q, \qquad w = \partial S(q, J)/\partial J \tag{96}$$

Hamilton's equations of motion in the action-angle representation are then[15,16]

$$\begin{aligned} \dot{w}_i &= \partial \tilde{H}(J_i)/\partial J_i = \omega_i(\text{const}) = \nu_i \Delta w_i(\text{const}); & w_i &= \omega_i t + \text{const} \\ \dot{J}_i &= -\partial \tilde{H}(J_i)/\partial w_i = 0, & J_i &= \text{const} \end{aligned} \tag{97}$$

where the transformed Hamiltonian $\tilde{H}$, whose value E is preserved by the canonical transformation, depends only on the action variables J_i, which now become constants of the motion. The cyclic angle variables w_i are periodic over a range Δw_i with angular frequency ω_i and natural frequency $\nu_i = \omega_i / \Delta w_i$. When Δw_i extends to 2π such that w_i is identified as a real angle, the resulting action-angle set (J_i, w_i) with $\nu_i = \omega_i / 2\pi$ is more suitable for modern quantal

development than the set (J', w_i') with $\nu_i = \omega_i'$, where ω_i', with a $[0 \rightarrow 1]$ range, is customarily used in most treatises of classical mechanics.[15,16] The action integral A_i of (95) is of course invariant to either choice so that the corresponding action variables are related by $J_i = J_i'/2\pi$.

For spherically symmetric interactions $V(r)$ (central forces), the angular frequencies ω_θ and ω_ϕ, obtained from the action set (J_r, J_θ, J_ϕ) associated with $\mathbf{r}(r, \theta, \phi)$ in spherical polar coordinates, are degenerate such that $E \equiv E(J_r, J_\theta + J_\phi)$, where the sum $(J_\theta + J_\phi)$ is the total conserved angular momentum. For a Coulomb field - the Kepler problem[16] - the motion is fully degenerate $(\omega_r = \omega_\theta = \omega_\phi)$ with $E \equiv E(J_r + J_\theta + J_\phi)$ and the orbit is closed. This full degeneracy may be eliminated by transformation to a new set of "*proper*" action variables $\mathbf{J}(J_\phi, J_\phi + J_\theta, J_\phi + J_\theta + J_r)$ and angle variables $\mathbf{w}(w_\phi - w_\theta, w_\theta - w_r, w_r)$ peculiar to the Coulomb problem. Thus application of the Bohr quantization rule (95) to (J_r, J_θ, J_ϕ) associated with libration variables (r, θ) and rotation variable ϕ yields, with $\Delta w_i = 2\pi$, the proper $(\mathbf{J}, \mathbf{w})$ representation:

$$\begin{aligned}
&J_m \equiv J_\phi = m\hbar, && w_m = w_\phi - w_\theta = \phi_E(\text{const}) \\
&J_l \equiv (J_\phi + J_\theta) = (m + n_\theta + \tfrac{1}{2})\hbar \equiv (l + \tfrac{1}{2})\hbar, && w_l = w_\theta - w_r = \psi_E(\text{const}) \\
&J_n = (J_\phi + J_\theta + J_r) = (m + n_\theta + n_r + 1)\hbar \equiv n\hbar, && w_n = w_r = (\partial E/\partial J_n)\, t + \delta \\
&J_m/J_l = \cos\theta_E, && \epsilon^2 = 1 - (J_l/J_n)^2
\end{aligned} \tag{98}$$

where $|m| = 0, 1, \ldots, l$; $l = 0, 1, \ldots, n$; $n = 1, 2, \ldots, \infty$; δ is a constant phase; and ϵ the eccentricity of the elliptical orbit. The new actions (J_n, J_l, J_m) can therefore be associated with quantum numbers (n, l, m), which are principal, angular momentum, and azimuthal, respectively, with the proper range of permitted values. For spherical symmetric $V(r)$, the orbit is confined to a plane. The action J_m is the constant component of the total angular momentum along a fixed Z axis and its conjugate angle w_m (fixed for constant m) is the Euler angle $\phi_E(0 \rightarrow 2\pi)$ between the line of nodes (the intersection of the plane of the orbit with the equatorial fixed XY plane) and the fixed X axis. The angle w_l conjugate to J_l is the Euler angle ψ_E between the line of nodes and some direction (in the orbit plane of the particle) usually taken as the direction of the perihelion (or perigee), which is fixed only for a Coulomb interaction. The remaining Euler angle θ_E is $\cos^{-1}(J_m/J_l)$, which is fixed for a given l and m. Hence the orientation of the orbit w.r.t. a fixed XYZ reference is defined by l and m. The remaining action J_n for a particle of reduced mass μ moving in $V(r)$ is[16]

$$J_n = \oint [2\mu(E - V(r)) - J_l^2/r^2]^{1/2}\, dr \tag{99}$$

such that $E(J_n, J_l)$. When V is $-e^2/r$, then (99) and (97) yield

$$E(J_n) = -\frac{\hbar^2}{J_n^2}\left(\frac{e^2}{2a_0}\right), \qquad \omega_n = \frac{\partial E}{\partial J_n} = n^{-3}\left(\frac{e^2}{\hbar a_0}\right) \tag{100}$$

such that for fixed n (and J_n) the particle moves in its bound orbit with a constant angular frequency ω_n. When $V(r)$ departs from pure Coulomb, a precession of the perihelion in the orbit plane occurs with angular frequency $\dot{\psi}_E$. Whereas the time-dependent $\mathbf{w}(t)$ are given by (97) and (100), the orbit $q(\mathbf{w})$ is obtained from (96).

The Bohr–Sommerfeld quantization rule (95) can now be exploited to establish the following correspondences between properties of classical motion and the quantum-mechanical observables:

1. It provides the general distribution of energy levels in the high-n spectrum, *the Bohr correspondence principle*.
2. It can be used to obtain *Heisenberg's correspondence principle*, which furnishes a powerful technique for the evaluation of various matrix elements involving highly excited states (nl) such as oscillator strengths, inelastic form factors, interaction matrix elements $V_{if}(\mathbf{R})$, S-matrix elements S_{ij}, etc., which occur in quantal and semiclassical treatments of scattering.

In the second case, the required quantal matrix element $\langle\phi_i(\mathbf{r})|V(\mathbf{r},\mathbf{R})|\phi_j(\mathbf{r})\rangle$, for example, is expressed as a given Fourier component of the static interaction $V(\mathbf{R}(t),\mathbf{r}(t))$ evaluated along a mean internal classical orbit $\mathbf{r}(t)$ for the Rydberg electron. When this classical $\mathbf{r}$ motion is periodic, the classical orbits $\mathbf{r}(\theta,\phi)$ and frequencies ω_i can be solved by the introduction of action-angle variables $(\mathbf{J},\mathbf{w})$ such that the internal $\mathbf{r}$ motion can then be quantized by replacing the action $\mathbf{J}$ by $2\pi(\mathbf{n}+\frac{1}{2})\hbar$, a procedure that provides, according to Sommerfeld, "the royal road to quantization," as quoted in Ref. 16 or else helps "sew the quantal flesh on classical bones."[34] Another advantage to the action-angle representation of the Rydberg atom in state $|nlm\rangle$ is that five of the six $(\mathbf{J},\mathbf{w})$ variables are constant, so that any small departures from a pure Coulomb field can be described very efficiently in terms of precession w.r.t. the angular variables.

11.4b. Bohr and Heisenberg correspondence principles

For large n, the energy separation ΔE between adjacent levels is small compared with the energies E_n, E_{n+1} of the levels, so that, for motion in one dimension, (95) applied to each level yields, upon subtraction,

$$\Delta E \oint (\partial p_i/\partial H_0)\, dq_i = \Delta E \oint dq_i/\dot{q}_i = \Delta E\, T_i \simeq 2\pi\hbar \tag{101}$$

where T_i is the classical period $(2\pi/\omega_i)$ for motion with angular frequency ω_i and where H_0 is the Hamiltonian. Hence, in a given range Δn of the quasi-classical spectrum, the neighboring levels are approximately equidistant by

$\hbar\omega_i$ such that the separation between any two levels n and $n+s$ within the range Δn is given by

$$E_{n+s} - E_n = h\nu_{n+s,n} \simeq s\hbar\omega_n \qquad (s = 1, 2, \ldots, \ll n) \tag{102a}$$

which is *Bohr's correspondence* between the line emission frequency $\nu_{n+s,n}$ and the angular frequency ω_n of classical orbital motion.

Use of Taylor's expansion yields, for quantal hydrogenic systems,

$$E_{n+s} - E_n = s\hbar\omega_n[1 - \tfrac{3}{2}(s/n) + 4(s/n)^2 + \cdots] \tag{102b}$$

which agrees with (102a) when $s \ll n$. This principle is easily extended to include D dimensions by adopting vector notation $\boldsymbol{\omega} \equiv \{\omega_i\}$, $\mathbf{n} \equiv \{n_i\} = (n, l, m, \ldots)$ and $\mathbf{s}(n'-n, l'-l, m'-m, \ldots)$. From (97), with angular range $\Delta\omega_i$ as 2π and (95)

$$\partial E/\partial n_i = \hbar\omega_i \tag{103}$$

such that the energy separation of levels $(n'l'm')$ and (nlm) is

$$\hbar\omega_{\mathbf{n}'\mathbf{n}} = E(\mathbf{n}') - E(\mathbf{n}) = \sum_{i=1}^{D} \Delta n_i\,(\partial E/\partial n_i) = \hbar\mathbf{s}\cdot\boldsymbol{\omega} \tag{104}$$

The number of states with quantum numbers in the range $\Delta\mathbf{n}$ is

$$\Delta N = \prod_{i=1}^{D} \Delta n_i = \prod_{i=1}^{D} (\Delta J_i\,\Delta w_i)/(2\pi\hbar)^D = \prod_{i=1}^{D} (\Delta p_i\,\Delta q_i)/(2\pi\hbar)^D \tag{105}$$

because the $(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{J}, \mathbf{w})$ transformation is canonical, which, therefore, implies invariance of the corresponding elements of phase space. Each quantum state of a system with D degrees of freedom occupies a cell of phase volume $(2\pi\hbar)^D$, as expected.

The mean value $\bar{F}$ of any physical quantity $F(q)$ in any quantum state Ψ tends, in the classical limit, to the classical value of that quantity *provided* that the quantum state itself can be described in the same limit by classical motion of the particle in a definite path. On expanding Ψ in terms of the quantal stationary states Ψ_n of the system with expansion coefficients a_n,

$$\bar{F} = \langle\Psi|F|\Psi\rangle = \sum_n \sum_m a_m^* a_n F_{mn}^{(q)} \exp(i\omega_{mn} t) \tag{106}$$

where $F_{mn}^{(q)}$ are the required quantal matrix elements between the time-independent states ϕ_n. With correspondence (104) used for ω_{mn} in (106) and with $s = n - m$,

$$\bar{F} = \sum_{n=1}^{\infty} \sum_{s=-\infty}^{n-1} a_{n-s}^* a_n F_{n-s,n}^{(q)} \exp(-is\omega t) \tag{107}$$

Although the elements $F_{n-s,n}$ decrease rapidly as $|s|$ increases, they exhibit only a slow variation with n for s fixed within some small range $\Delta n \ll n$ about n, so that

$$\bar{F} = \sum_n |a_n|^2 \sum_{s=-\infty}^{\infty} F_s^{(q)} \exp(-is\omega t); \qquad F_s = F_{\bar{n}-s,\bar{n}} \tag{108}$$

where $\bar{n}$ is some mean value of n in the range Δn. Because $\bar{F}$ in the classical limit tends to $F^c(t)$ and $\sum_n |a_n|^2 = 1$, the quantal matrix elements F_{mn} reduce in the classical limit to the components F_{n-m} obtained in the expansion of the classical function $F^c(t)$ as a Fourier series, i.e.,

$$\begin{aligned} F_{mn}^{(q)}(\mathbf{R}) &= \int_0^{\infty} \phi_m^*(r) F(r, \mathbf{R}) \phi_n(r)\, dr \simeq F_s^{(c)} \\ &= (\omega/2\pi) \int_0^{2\pi/\omega} F^{(c)}(r(t)) \exp(is\omega t)\, dt \end{aligned} \tag{109}$$

where $r(t)$ is the classical variation of r with time t. When bounded motion for several degrees of freedom can be described by a separable Hamiltonian (e.g., Kepler problem), the classical position $\mathbf{r}$ is periodic in the angle variables $\mathbf{w}$ and separates as a Fourier series[16]

$$\mathbf{r}(t) = \sum_{\text{all } \mathbf{s}} \mathbf{r}_s(\mathbf{J}) \exp(-i\mathbf{s} \cdot \mathbf{w}), \qquad \mathbf{w} = \omega t + \boldsymbol{\delta} \tag{110}$$

where the components of order $+s$ and $-s$ result in emission and absorption of radiation at frequency $s\omega$. Any classical function $F^c(\mathbf{r})$ is also periodic in $\mathbf{r}$, i.e.,

$$F^c(\mathbf{r}(t)) = \sum_{\mathbf{s}} F_{\mathbf{s}}^c(\mathbf{J}) \exp(-i\mathbf{s} \cdot \mathbf{w}) \tag{111}$$

where the Fourier coefficients in three dimensions yield the quantal matrix elements

$$F_{\mathbf{n}'\mathbf{n}}^{(q)} \simeq F_{\mathbf{s}}^c(\mathbf{J}) = (2\pi)^{-3} \int F^c(\mathbf{r}(\mathbf{J}, \mathbf{w})) \exp(i\mathbf{s} \cdot \mathbf{w})\, d\mathbf{w}, \tag{112}$$

in the classical limit, where $\mathbf{n} \equiv (n, l, m)$ and $\mathbf{s} = (\mathbf{n} - \mathbf{n}')$. Expressions (109) and (112) represent *the Heisenberg correspondence principle* for one and three internal degrees of freedom, respectively. When $\mathbf{s}$ is zero, the expectation value of F is then the average of F over the classical orbit associated with quantum numbers (nlm). A nondiagonal element is a similar average of $F\exp(i\Delta S/\hbar)$, where ΔS is the difference between the actions $J_n w_n$ and $J_{n'} w_{n'}$ associated with the initial and final classical orbits at a given time.

For example,

$$\begin{aligned} &\sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} |\langle n'l'm'|F(\mathbf{r})|nlm\rangle|^2 \\ &\quad = (2\pi)^{-6} \sum_{m=-l}^{l} \sum_{\Delta m} \int F(\mathbf{J}, \mathbf{w}) F^*(\mathbf{J}, \mathbf{w}') \exp[i\mathbf{s} \cdot (\mathbf{w} - \mathbf{w}')]\, d\mathbf{w}\, d\mathbf{w}' \end{aligned} \tag{113}$$

with $d\mathbf{w}=(dw_n, dw_l, dw_m)$ and $\mathbf{s}=-(\Delta n, \Delta l, \Delta m)$, which, on summation over Δm, reduces with the aid of (98) to

$$\sum_m \sum_{m'} |\langle n'l'm'|F(\mathbf{r})|nlm\rangle|^2$$

$$= \frac{(l+\frac{1}{2})}{(2\pi)^5} \int_{-1}^{+1} d(\cos\theta_E) \int_0^{2\pi} d\phi_E \left| \int F(\mathbf{J},\mathbf{w}) \exp[-i(\Delta n\, w_n + \Delta l \psi_E)\, dw_n\, d\psi_E \right|^2 \tag{114}$$

Similarly, on summing (114) over all l and l' and averaging over the n^2 initial states, we have

$$|\langle n'|F(\mathbf{r})|n\rangle|^2$$

$$= (2\pi)^{-4} \int_0^1 d\epsilon^2 \int_{-1}^{+1} d(\cos\theta_E) \int_0^{2\pi} d\psi_E \int_0^{2\pi} d\phi_E \left| \int F(\mathbf{r}(\mathbf{J},\mathbf{w})) \exp(-i\Delta n\, w_n)\, dw_n \right|^2 \tag{115}$$

which is an average over w_n in the plane of the orbit, over orientations (ϕ_E, different m or lines of nodes; ψ_E, different l or perihelions; θ_E, different planes of orbit for fixed line of nodes or directions of total angular momentum) of that plane, and over all possible eccentricities (shapes) ϵ^2 of the orbits. Thus (115) represents an average of the one-dimensional result (109) over a microcanonical distribution, which assumes equal weighting of each of the n^2 states (lm) and uniform distribution of ϵ^2 between 0 and 1. Evaluation of the w_n integral in (115) or (109) can be achieved for bounded motion under a pure Coulomb attraction via the following parameter form of the classical orbits:[35]

$$r = a_n(1-\epsilon\cos\chi), \quad w_n = \omega_n t + \delta = \omega_n \tau = \chi - \epsilon\sin\chi$$

$$x = a_n(\cos\chi - \epsilon), \quad y = a_n(1-\epsilon^2)^{1/2}\sin\chi, \quad \tan\tfrac{1}{2}w_n = \left(\frac{1+\epsilon}{1-\epsilon}\right)^{1/2} \tan\tfrac{1}{2}\chi \tag{116}$$

where χ is the eccentric anomaly that varies between 0 and 2π (0 at perihelion and π at aphelion) during a full revolution of the angle w_n and τ the epoch or time measured from the instant when the particle is at perihelion [perigee, $\chi=0$, $r=a_n(1-\epsilon)$]. The semimajor axis a_n, eccentricity ϵ, and angular frequency ω_n for the classical orbit appropriate to fixed n and l are

$$a_n = n^2 a_0, \qquad \epsilon = [1-(l+\tfrac{1}{2})^2/n^2]^{1/2}, \qquad \omega_n = n^{-3}(e^2/a_0\hbar) \tag{117}$$

11.4c. Correspondence approximations for atomic properties and collision amplitudes

By selection of different observables F, a variety of correspondence limits can be obtained and expressed as further correspondence principles. For example,

the mean power spontaneously emitted in a radiative transition $n' \to n$ or the mean power absorbed from incident radiation due to induced upward and downward transitions $n' \leftrightarrows n$ can be identified, respectively, with the mean emitted or absorbed power determined by the classical Fourier components of order s $(=n-n')$ and $-s$ of the dipole moment.[13,36]

Formulae for the classical intensity of the components of dipole radiation are given in standard textbooks of classical radiation theory.[35,37] Also, the classical energy $\Delta E^{(c)}$ transferred to a Rydberg atom by an incident charged particle is, with the aid of (111) and (112),

$$\Delta E^{(c)} = \int_{-\infty}^{\infty} \mathbf{F} \cdot \mathbf{v}\, dt = \sum_{s=-\infty}^{\infty} \mathbf{v}_s \cdot \int_{-\infty}^{\infty} \mathbf{F}(t) \exp(-is\omega t)\, dt$$

$$= \sum_s \Delta E_s^{(c)} \simeq \sum_{n'} \overline{\Delta E}_{n'n}^{(q)} \tag{118}$$

which equals the mean energy transferred in quantal upward and downward transitions $n \leftrightarrows n'$ summed over all final states n'. Here $\mathbf{v}(\mathbf{r}(t))$ is the classical velocity of the Rydberg electron at $\mathbf{r}$ and $\mathbf{F}$ the electric force provided at the electron by the incident charge Ze of impact parameter ρ. When $\rho \gg r$, then F remains effectively constant over the atom (dipole approximation) and the preceding Fourier transforms (of momentum transfers) $\mathbf{F}_s$ of $\mathbf{F}$ can be readily obtained[37] in terms of modified Bessel functions $K_{0,1}$ as

$$\mathbf{F}_s(\omega) = \int_{-\infty}^{\infty} \mathbf{F}(t) \exp(-is\omega t)\, dt$$

$$= 2\left(\frac{Ze^2}{v\rho}\right)\left(\frac{\omega s\rho}{v}\right)\left[-iK_0\left(\frac{s\omega\rho}{v}\right)\hat{\mathbf{k}} + K_1\left(\frac{s\omega\rho}{v}\right)\hat{\boldsymbol{\rho}}\right] \tag{119}$$

where $\hat{\mathbf{k}}$ is the direction of incidence normal to the impact-parameter direction $\hat{\boldsymbol{\rho}}$. Equation (119) can then be used in (118) to determine the energy transferred to a charge bound harmonically[37] or by a Coulomb attraction for which $\mathbf{v}_s$, with the aid of (116), is[35]

$$\mathbf{v}_s = -is\omega_n \mathbf{r}_s = \omega_n a_n\{-iJ_s'(s\epsilon)\hat{\mathbf{i}} + [(1-\epsilon^2)^{1/2}/\epsilon]J_s(s\epsilon)\hat{\mathbf{j}}\} \tag{120}$$

where $\hat{\mathbf{i}}$, directed toward the perihelion, and $\hat{\mathbf{j}}$ denote directions of the XY axes in the orbit plane and J_s' the differentiation of the Bessel function J_s with respect to its argument. The mean energy transferred $\langle \Delta E^{(q)} \rangle$ in $n \leftrightarrows n'$ collisional transitions is therefore $F_s(\omega_n) v_s$, with $s = n - n'$ in the appropriate correspondence limit of weak interaction for simultaneous validity of both classical and quantal perturbation theory (small variation to classical orbit and small transition probability $P_{nn'}$, respectively). By paying attention to detailed balancing between upward and downward transition probabilities, Percival and Richards,[38] with the use of (118)–(120), were able to show that at asymptotic impact energies E the cross section for charged-particle–Rydberg collisions varies as $E^{-1} \ln E$, in contrast to the E^{-1} variation obtained from a clas-

sical theory (binary encounter, for example) based on the full classical energy transfer $\Delta E^{(c)}$. Correspondence is, therefore, preserved, provided classical probabilities are deduced from the Fourier components $\Delta E_s^{(c)}$ of $\Delta E^{(c)}$ rather than from $\Delta E^{(c)}$ alone.[38] For Rydberg collisions at lower energies, contributions from higher multipoles tend to dominate the cross sections (see Sect. 11.2). The ln E term is significant therefore only in the high-energy limit where the proper energy change is given by the individual components $\mathbf{F}_s \cdot \mathbf{v}_s$ of (118).

Atomic properties

The accuracy of results obtained from Heisenberg's principle can be tested, when possible, by direct comparison with quantal results. It follows from (120) that the dipole matrix element summed over all states m and m' and averaged over the $(2l+1)$ initial states is

$$|\langle n'l \pm 1|\mathbf{r}|nl\rangle|_c^2 = \frac{3}{2} a_n^2 \frac{1+(s/n)}{3s} [J_s'(s\bar{\epsilon}) \pm (\bar{\epsilon}^{-2}-1)^{1/2} J_s(s\bar{\epsilon})]^2 g_c(s) \qquad (121)$$

where $\bar{\epsilon}$ is the eccentricity (117) appropriate to some averaged $\tilde{l}$ and $\tilde{n}$ and

$$g_c(s) = \frac{2n'}{n+n'} \frac{\tilde{n}}{n} \qquad (122)$$

On averaging over all n^2 initial states $|lm\rangle$ and summing over all final states i.e., integrating (121) over ϵ^2 between 0 and 1, then

$$|\langle n'|\mathbf{r}|n\rangle|_c^2 = \frac{3}{2} a_n^2 \left(1 + \frac{s}{n}\right) \frac{4}{3s^3} J_s(s) J_s'(s) g_c(s) \qquad (123)$$

to be compared with the quantal results of Menzel,[39] who gives (123) with g_c replaced by $1+(3s/2n)+[A(s)/n^2]$, where $A(s)$ is of order unity. For a mean orbit, $\tilde{n}=\frac{1}{2}(n+n')$ and g_c is then $1+(s/n)$. For $\tilde{n}=2n'^2/(n+n')$, which ensures detailed balance between the oscillator strengths

$$n^2 f_{nn'} = [\tfrac{2}{3}(m/\hbar^2) E_{n'n}] n^2 |\langle n'|\mathbf{r}|n\rangle|^2 = -n'^2 f_{n'n} \qquad (124)$$

for emission and absorption, then g_c is $1+(2s/n)+(2s^2/4n^2)$.[40] Use of asymptotic J_s in (123) for large s but $\ll n$ yields the Gaunt-Kramers result[41]

$$f_{nn'} \simeq (0.49/2n^2)/(nn'\omega)^3, \qquad 2\omega = n^{-2} - n'^{-2} \qquad (125)$$

and provides a reasonable approximation for the oscillator strength between two excited levels even for small s. On extrapolating n' to a continuum state of energy ϵ,

$$df(n,\epsilon)/d\epsilon \simeq (0.49/2n^2)/(n\omega)^3 \qquad (126)$$

Upon use of the oscillator strength sum rule, we note, therefore, that most of the oscillator strength from an excited level n is essentially exhausted by transitions to bound levels and that little remains $(\sim 0.49/n)$ for transitions to

the continuum (a feature responsible even for the abnormally small cross sections for the photoionization of metastable rare gas atoms).[42]

Further applications of the correspondence principle to determination of various matrix elements are given by Naccache[43] and de Prunelé.[44] In conclusion, agreement between quantal and correspondence results are, in general, obtained when $s \ll n$, $n' \gg 1$. However, de Prunelé[44] pointed out that a further sufficient condition for validity is that $F(\mathbf{r}, \mathbf{p})$ must not significantly weight the classical inaccessible region. If this latter condition is not fulfilled, then an appropriate extension of the semiclassical procedure given in Sect. 11.4 is valuable.

Collision amplitudes

Use of the Bohr and Heisenberg correspondences (102) and (112), respectively, for ω_{fi} and V_{fi} in the first-order semiclassical result (94) yields

$$S_{fi}^{(1)} = -\frac{i}{\hbar}\left(\frac{\omega}{2\pi}\right)\int_{-\infty}^{\infty} dt \int_0^{2\pi/\omega} V(\mathbf{R}(t), r(t_1)) \exp[is\omega(t_1 - t)]\, dt_1$$

$$= -\frac{i}{\hbar}\left(\frac{\omega}{2\pi}\right)\int_0^{2\pi/\omega} dt_c \int_{-\infty}^{\infty} V(\mathbf{R}(t), r(t + t_c)) \exp(is\omega t_c)\, dt, \qquad s = i - f \tag{127}$$

in which the external (projectile) motion along a classical path $\mathbf{R}(t)$ is correlated to the classical internal motion of the Rydberg electron in the orbit $r(t_c)$. When $S_{fi}^{(1)}$ is substituted for a_f in (53) with its straight-line external trajectory, the resulting cross sections are valid only (Sect. 11.3) in the heavy-particle–high-energy limit for collisions of ions, neutrals, and electrons with Rydberg atoms.

For the sudden approximation (92), F in (112) is taken as $S^{(S)}$ such that

$$S_{fi}^{(S)} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} dt_c \exp\left[is\omega t_c - \frac{i}{\hbar}\int_{-\infty}^{\infty} V(\mathbf{R}(t), r(t_c))\, dt\right] \tag{128}$$

directly, where there is now no correlation between internal and external motions in accordance with the impulse assumption. It is tempting to replace $r(t_c)$ in (128) by $r(t+t_c)$ in order to obtain an expression that yields both the correct sudden and weak-interaction limits. Percival and Richards[5] introduced such correlations into (128) by substituting the sequential relation

$$U(t_N, t_0) = \prod_{j=0}^{N-1} \mathbf{U}(t_{j+1}, t_j), \qquad t_j = t_0 + j\,\Delta t \tag{129}$$

between the evolution operators for small time intervals Δt into (80), which they then solved to first order in V_1 to give, upon use of Heisenberg's correspondence, the overall matrix element that reduces (after detailed analysis) to

$$U_{fi}(T,t_0) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega}\prod_{j=0}^{N-1}\left[1 - \frac{i\Delta t}{\hbar}V(\mathbf{R}(t_j), r(t_j+\tau))\right]\exp(is\omega\tau)\,d\tau \quad (130)$$

where $s=i-f$. Upon replacing the bracketed term by an exponential (equivalent to first order in Δt) and by letting $N\to\infty$ such that the product is converted to an integral, Percival and Richards[5] obtained the following collision amplitude:

$$S_{fi}^{(SC)} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega}\exp\left[i(s\omega t_c) - \frac{i}{\hbar}\int_{-\infty}^{\infty}V(\mathbf{R}(t), r(t+t_c))\,dt\right]dt_c \quad (131)$$

which they termed the *strong correspondence principle.* This result indeed exhibits the desired characteristics of (127) for weak V and of (128) for sudden collision.

An interesting and rigorous theoretical generalization of (128) that includes diabatic effects and a three-dimensional electron orbit will now be presented.

11.4d. Equivalent oscillator theorem

The main advantage underlying the use of the action-angle representation in quantum mechanics is that the unperturbed Hamiltonian $H_0(\mathbf{J})$ depends only on $\mathbf{J}$, which is therefore conserved (because $\mathbf{w}$ is cyclic). The action operator $\hat{\mathbf{J}}$ is defined with the aid of its associated quantal commutator

$$[\hat{J}_i, w_i] = -i\hbar \quad (132)$$

and of (95) as

$$\hat{J}_i\phi_{n_i}(w_i) = \left[-i\hbar\frac{\partial}{\partial w_i} + \alpha_i\hbar\right]\phi_{n_i}(w_i) = J_i\phi_{n_i} = (n_i+\alpha_i)\hbar \quad (133)$$

such that

$$\phi_{\mathbf{n}}(\mathbf{w}) = (2\pi)^{-3/2}\exp(i\mathbf{n}\cdot\mathbf{w}) \quad (134)$$

in three dimensions. Hence the quantal matrix elements $F_{\mathbf{n}'\mathbf{n}}$ of $F(\mathbf{n})$ given by Heisenberg's correspondence principle (112) are simply the matrix elements of F in the action-angle representation. Because the total energy E_n and time t are also conjugate variables, the time-dependent wave function in the action-angle representation is

$$\phi_{\mathbf{n}}(\mathbf{w},t) = \phi_n(\mathbf{w})\exp(-iE_nt/\hbar) \quad (135)$$

The "classical path" equation (66) in this representation is

$$[H_0(\hat{\mathbf{J}}) + V(\mathbf{J},\mathbf{w},t)]\Psi(\mathbf{w},t) = i\hbar\,\partial\Psi(\mathbf{w},t)/\partial t \quad (136)$$

for which the system wave function is expanded in terms of the unperturbed basis set $\{\phi_n(\mathbf{w},t)\}$ as

$$\Psi(\mathbf{w},t) = \sum_n a_n(t)\phi_n(\mathbf{w})\exp(-iE_nt/\hbar) \quad (137)$$

The transition amplitudes [or $S_{fi}(t \to \infty)$] then satisfy

$$i\hbar\, \partial a_f/\partial t = \sum_n a_n(t) V_{fn}(t) \exp(i\omega_{fn} t) = \sum_{d=-f} a_{d+f}(t) V_d(t) \exp(-id\omega t) \tag{138}$$

in which the Bohr and Heisenberg correspondence principles (102) and (112) have been invoked, respectively, for $\omega_{fn} = (f-n)\omega \equiv -d\omega$ and for V_{fn}, i.e.,

$$V_{fn}(t) = V_d(t) = (2\pi)^{-3} \int_0^{2\pi} V(\mathbf{w}', t) \exp(i\mathbf{d} \cdot \mathbf{w}')\, d\mathbf{w}', \qquad \mathbf{d} = \mathbf{n} - \mathbf{f} \tag{139}$$

Hence set (138) can be written as

$$i\hbar\, \partial a_f/\partial t = \sum_{d=-f} a_{d+f}(t) V_d'(t) \tag{140}$$

where, on replacing $(\mathbf{w} - \omega t)$ by the angle variable $\mathbf{w}$,

$$\begin{aligned} V_d'(t) = \exp(-id\omega t) V_d(t) &= (2\pi)^{-3} \int_0^{2\pi} V(\mathbf{w} + \omega t, t) \exp(i\mathbf{d} \cdot \mathbf{w})\, d\mathbf{w} \\ &\equiv \langle \phi_f(\mathbf{w}) | V(\mathbf{w} + \omega t, t) | \phi_n(\mathbf{w}) \rangle \end{aligned} \tag{141}$$

The operator $V(\mathbf{w} + \omega t, t)$ commutes at different times t_1 and t_2 such that set (140) can be solved exactly (Sect. 11.3a), subject to $a_f(t \to -\infty) = \delta_{fi}$, to yield

$$a_f(t) = \left\langle \phi_f(\mathbf{w}) \middle| \exp\left[-(i/\hbar) \int_{-\infty}^{t} V(\mathbf{w} + \omega t, t)\, dt \right] \middle| \phi_i(\mathbf{w}) \right\rangle \tag{142}$$

and hence the transition probability amplitude is

$$S_{\mathbf{n}'\mathbf{n}} = a_{\mathbf{n}'}(t \to \infty) = (2\pi)^{-3} \int_0^{2\pi} d\mathbf{w} \exp\left[i\mathbf{s} \cdot \mathbf{w} - (i/\hbar) \int_{-\infty}^{\infty} V(\mathbf{w} + \omega t, t)\, dt \right] \tag{143}$$

where $\mathbf{s} = \mathbf{n} - \mathbf{n}'$ for $\mathbf{n}(nlm) \to \mathbf{n}'(n'l'm')$ transitions. This exact expression follows directly from (136) under the conditions of Bohr and Heisenberg correspondence, which, therefore, expose the key - the Fourier index d in (139) being equal to the angular index d in $\exp(-id\omega t)$ of (138) - which is essential for an exact solution. Because w_n of $\mathbf{w}(w_n, w_l, w_m)$ is ωt_e, where t_e is the time describing the internal Rydberg electron in its orbit, we note that the action integral over the external classical path contains, via $(\mathbf{w} + \omega t)$, a time evolution that expresses coupling between the classical internal and external motions, i.e., diabatic effects are acknowledged.

In the limit of weak interaction, (i.e., when $V\tau_c \ll 1$ where τ_c is the collision time),

$$S_{\mathbf{n}',\mathbf{n}}^{(B)} = (2\pi)^{-3} (-i/\hbar) \int_0^{2\pi} d\mathbf{w} \exp(i\mathbf{s} \cdot \mathbf{w}) \int_{-\infty}^{\infty} V(\mathbf{w} + \omega t, t)\, dt \tag{144}$$

which is the equivalent of the Born approximation to (138) and which also correlates the internal and external classical motions of the Rydberg electron and projectile, respectively.

In the impulse limit, i.e., when $\tau_c \ll w/\omega \simeq 2\pi/\omega = T_e$ the orbital period,

$$S^{(S)}_{\mathbf{n}',\mathbf{n}} = (2\pi)^{-3} \int_0^{2\pi} d\mathbf{w} \exp\left[i\mathbf{s}\cdot\mathbf{w} - (i/\hbar) \int_{-\infty}^{\infty} V(\mathbf{w},t)\, dt \right] \tag{145}$$

which is the equivalent of the sudden approximation that neglects ω_{fn} in (138). We note also that (145) contains no correlation between the internal and external motions in accordance with the impulse assumption that the Rydberg electron remains fixed during the encounter. When (145) is inserted for a_f in (50) and (53), then expressions identical with the Glauber approximation are obtained.[8]

Because the only assumptions underlying (143) are Bohr correspondence (equally spaced levels as in a harmonic oscillator) and Heisenberg correspondence for the interaction matrix elements, the basic expression (138) yields what we term the *equivalent oscillator theorem* for the collisional transition amplitudes. Similar or related expressions have also been obtained less directly by other means (see Sects. 11.4e and 11.4f).[4-7]

The classical limit to (143) is obtained by evaluating the integral by the method of stationary phase, which is located at $\mathbf{w}$, given by

$$\mathbf{s}\hbar = \frac{\partial}{\partial \mathbf{w}} \left[\int_{-\infty}^{\infty} V(\mathbf{J},\mathbf{w},t)\, dt \right] = -\int_{-\infty}^{\infty} \mathbf{F}(\mathbf{J},\mathbf{w},t)\, dt = (\mathbf{n}-\mathbf{n}')\hbar \tag{146}$$

where $\mathbf{F}$ is the generalized force $-\nabla_{\mathbf{w}} V$. Thus, in the classical limit, the change $(\mathbf{n}'-\mathbf{n})\hbar$ in the generalized momentum $\mathbf{J}$ is given by the impulse of the generalized force. The transition amplitude (143) is therefore

$$S_{\mathbf{n}'\mathbf{n}} = (2\pi)^{-3} \int_0^{2\pi} d\mathbf{w}\, \delta\left[\mathbf{s}\hbar + \int_{-\infty}^{\infty} F(\mathbf{J},\mathbf{w}+\omega t,t)\, dt \right] \tag{147}$$

in accordance with the classical perturbation theory.

11.4e. Semiclassical wave functions, correspondences, and perturbation theory

It is well known that the WKB-bound state wave functions for classical accessible and inaccessible regions when matched result directly in Bohr's quantization rule (95).[30] It is, therefore, of interest to develop the radial matrix elements appropriate to the radial WKB wave function

$$\chi_{nl}(r) = \left(\frac{1}{\pi} \frac{\partial p_r}{\partial J_r} \right)^{1/2} \exp\left[iS_{nl}(q_r, J_r)/\hbar + \frac{\pi}{4} \right] \tag{148}$$

where, for the classical accessible region, the radial generator of the canonical $(\mathbf{p},\mathbf{q} \rightarrow \mathbf{J},\mathbf{w})$ transformation that preserves the value E of the Hamiltonian $H(\mathbf{p},\mathbf{q}) = \tilde{H}(\mathbf{J}) = E$ in the action-angle $(\mathbf{J},\mathbf{w})$ representation is

$$S_{nl}(q_r, J_r) = \int p_r\, dq_r = \int_{r_1}^{r} \left\{ 2m[E_{nl} - V(r)] - \frac{(l+\frac{1}{2})^2\hbar^2}{r^2} \right\}^{1/2} dr \tag{149}$$

for a particle of mass m bound with energy E_{nl} by $V(r)$ between classical turning points $r_{1,2}$ given by $p_r^2(r_{1,2}) = 0$. This transformation is therefore governed by

$$\begin{aligned} \dot{w}_r &= \partial\tilde{H}(\mathbf{J})/\partial J_r \equiv \dot{q}_r\, \partial p_r/\partial J_r = \omega_n, & p_r &= \partial S(q_r, J_r)/\partial q_r \\ \dot{J}_r &= \partial\tilde{H}(\mathbf{J})/\partial w_r = 0, & w_r &= \partial S(q_r, J_r)/\partial J_r \end{aligned} \tag{150}$$

For each full revolution, the action phase (149) of χ_{nl} increases by the action integral

$$J_r\, \Delta w_r = 2\pi J_r = \oint p_r\, dq_r = S_{nl}(2\pi, J_r) \tag{151}$$

evaluated around a closed loop (denoted by 2π).

When the levels nl and $n'l'$ are close (i.e., $\Delta = (n_r - n_r') \ll n, n'$), then

$$S_{n'l'}(q_r, J_r') = S_{nl}(q_r, J_r) + (\partial S_{nl}/\partial J_r)\,(J_r' - J_r) + \cdots \tag{152}$$

which, with the aid of (98)

$$J_r = (n_r + \tfrac{1}{2})\hbar = (n - l - 1)\hbar, \qquad w_n = w_r \tag{153}$$

for a Rydberg atom, yields the eikonal difference

$$S_{nl}(q, J_r) - S_{n'l'}(q, J_r') = (\Delta n - \Delta l)\hbar\omega_n t, \qquad \Delta n = n' - n, \quad \Delta l = l' - l \tag{154}$$

Hence, with the aid of $\dot{w}_n$ in (148), the radial matrix element

$$\begin{aligned} F_{n'l',nl} &= \int_{r_1}^{r_1} \chi_{n'l'}^*(r) F(r) \chi_{nl}(r)\, dr \\ &= (1/2\pi) \oint F(r) \exp[i(\Delta n - \Delta l) w_n]\, dw_n \end{aligned} \tag{155}$$

such that the function

$$F(r) = \sum_{s=-\infty}^{\infty} F_{n'l',nl} \exp[-i(\Delta n - \Delta l) w_n] \tag{156}$$

which is equivalent to the Heisenberg correspondence principle for radial matrix elements. The angular portion of the three-dimensional matrix element $\langle \phi_{n'l'}(\mathbf{r}) | V(\mathbf{r}) | \phi_{nl}(\mathbf{r}) \rangle$ may be determined either quantum mechanically by standard angular momentum coupling theory involving $Y_{lm}(\hat{\mathbf{r}})$ or by the semiclassical angular equivalents to (148) and (155). Thus a full semiclassical analysis – (148) or its three-dimensional equivalent in (34) – leads directly to the equivalent oscillator theorem (143).

The semiclassical wave function over the classical accessible (q_1, q_2) and inaccessible regions are appropriate combinations of

$$\chi_{nl}(q) = \left(\frac{2\omega_n}{\pi^{1/2}p_r}\right)^{1/2} \sin\left[\frac{1}{\hbar}\int_{q_1}^{q} p\,dq + \frac{\pi}{4}\right], \qquad q \gg q_1$$

$$= \left(\frac{\omega_n}{2\pi^{1/2}|p_r|}\right)^{1/2} \exp\left[-\frac{1}{\hbar}\int_{q}^{q_1} |p|\,dq\right], \qquad q \ll q_1$$

$$= \pm\left(\frac{2\omega_n}{\pi^{1/2}p_r}\right)^{1/2} \sin\left[\frac{1}{\hbar}\int_{q}^{q_2} p\,dq + \frac{\pi}{4}\right], \qquad q \ll q_2$$

$$= \pm\left(\frac{\omega_n}{2\pi^{1/2}|p_r|}\right)^{1/2} \exp\left[-\frac{1}{\hbar}\int_{q_2}^{q} |p|\,dq\right], \qquad q \gg q_2 \qquad (157)$$

where the inequalities are satisfied within a few wavelengths. The sum of phases for a bound state equals $n_r\pi$ and Bohr's quantization (98) is recovered. Matrix elements of a function $F(p,q)$ that weights the classical inaccessible region significantly may then be determined by using (155) for the classical accessible region (which contains all the difficult oscillatory portion of the bound-state wave function) and the exponential increasing and decreasing $\chi_{nl}(q)$ in (157) for the inaccessible regions.

In the action-angle representation, the normalized wave function is

$$\chi_{nl}(w_r) = (2\pi)^{-1/2}\exp(iJ_r w_r/\hbar) = (2\pi)^{-1/2}\exp i[n - (l + \tfrac{1}{2})]w_n \qquad (158)$$

from which the wave function in the (p,q) representation is obtained from

$$\chi_{nl}(q) = \oint A_1(q, w_r)\chi_{nl}(w_r)\,dw_r \qquad (159)$$

where the transform A_1 is unitary, i.e.,

$$\int A_1^*(q, w_r')A_1(q, w_r)\,dq = \delta(w_r - w_r') \qquad (160)$$

to preserve orthonormality $\langle\chi_i|\chi_f\rangle = \delta_{if}$ in both representations. The quantal matrix elements

$$\langle\chi_{n'l'}(q)|F(q)|\chi_{nl}(q)\rangle = \oint \chi_{n'l'}^*(w_r)F(J_r, w_r)\chi_{nl}(w_r)\,dw_r \qquad (161)$$

are therefore the corresponding matrix elements in the action-angle $(\mathbf{J}, \mathbf{w})$ representation. Note that the transform A_1 for hydrogenic systems is simply the Fourier transform of the WKB semiclassical wave function (148).

Not only does the action-angle representation permit wave functions (134), (135) and (158) to have particularly simple forms but it also permits construction of a systematic perturbation procedure based on the Hamilton–Jacobi equation[15]

$$(\partial S/\partial t) + H_0(\partial S/\partial \mathbf{w}) + V(\mathbf{w}^0, \partial S/\partial \mathbf{w}, t) = 0 \qquad (162)$$

where $S(\mathbf{w}^0, \mathbf{J})$ is the generator of the canonical transformation from the "unperturbed" representation $(\mathbf{J}^0, \mathbf{w}^0)$ to the "perturbed" representation $(\mathbf{J}, \mathbf{w}^0)$ such that

$$\begin{aligned} \mathbf{J}^0 &= \partial S(\mathbf{w}^0, \mathbf{J})/\partial \mathbf{w}^0, \qquad \mathbf{w} = \partial S(\mathbf{w}^0, \mathbf{J})/\partial \mathbf{w}^0 \\ \dot{\mathbf{J}} &= -\partial H(\mathbf{J}, \mathbf{w})/\partial \mathbf{w}, \qquad \dot{\mathbf{w}} = \partial H(\mathbf{J}, \mathbf{w})/\partial \mathbf{J} \end{aligned} \tag{163}$$

where H, the total Hamiltonian $H_0(\mathbf{J}^0) + \lambda V(\mathbf{J}, \mathbf{w})$, is no longer a function of $\mathbf{J}$ alone. By expanding S as $S_0 + \lambda S_1 + \cdots$ and

$$\begin{aligned} H_0(\mathbf{J}) - H_0(\mathbf{J}^0) &= (\partial H_0/\partial \mathbf{J})_{\mathbf{J}^0} \cdot (\mathbf{J} - \mathbf{J}_0) + \cdots \\ &\equiv \lambda \sum_j (\partial H_0/\partial J_j)(\partial S_1/\partial w_j^0) + \cdots \end{aligned} \tag{164}$$

then the first two action terms are

$$S_0 = \mathbf{J}^0 \cdot \mathbf{w}^0 - E_n^0 t \tag{165}$$

and, provided S_1 is separable in the angle variables,

$$S_1(\mathbf{w}, t) = -\int_{-\infty}^{t} V(\mathbf{w} + \omega(t' - t), t')\, dt' \tag{166}$$

which is the solution of

$$(\partial S_1/\partial t) + \omega\,(\partial S_1/\partial \mathbf{w}) = -V(\mathbf{w}, t) \tag{167}$$

On using the semiclassical wave function for the system, the transition probability is, therefore,

$$P_{nn'} = (2\pi)^{-1} \lim_{t \to \infty} |\langle \exp i\mathbf{J}_{n'}^0 \cdot \mathbf{w}_{n'}^0 | \exp iS(\mathbf{J}, \mathbf{w}^0) \rangle|^2 \tag{168}$$

which, with S taken as $S_0 + S_1$, reduces to

$$P_{nn'} = \left| (2\pi)^{-3} \int_0^{2\pi} d\mathbf{w} \exp\left[i\mathbf{s} \cdot \mathbf{w} - (i/\hbar) \int_{-\infty}^{\infty} V(\mathbf{w} + \omega t, t)\, dt \right] \right|^2 \tag{169}$$

in agreement with (143). This result is essentially the three-dimensional generalization of the result obtained by Beigman et al.[4] for one degree of internal freedom.

Because semiclassical wave functions with Bohr's correspondence yield the Heisenberg correspondence directly and, when substituted into a classical path semiclassical treatment (34), yield the equivalent oscillator theorem (143), it is therefore consistent that the preceding perturbation treatment, based on the Hamilton–Jacobi equation, which is intimately related to (34) (see Sect. 11.3b), should yield similar results. Presynakov and Urnov[6] obtained for one degree of internal freedom a related "equally spaced levels" approximation

$$S_{n',n} = (2\pi)^{-1} \int_0^{2\pi} dw \exp\left[isw - (1/\hbar) \sum_k \int_{-\infty}^{\infty} V_k(t) \exp ik(\omega t + w)\, dt \right] \tag{170}$$

which reduces to the one-dimensional equivalent oscillator.[7]

From (130), or by expanding (169) to first order in V taken as the dipole interaction

$$V(\mathbf{R},\mathbf{r}) = -Z_p e^2(\mathbf{R}\cdot\mathbf{r}/R^3) \tag{171}$$

of a Rydberg atom of nuclear charge $Z_c e$ with a projectile of charge $Z_p e$, the collisional probability for $n \to n'$ transitions reduces, for large-impact parameters ρ, to[29]

$$P_{nn'}(\rho,v) = \left[n\left(\frac{Z_p}{Z_c}\right)\left(\frac{v_n}{v}\right)^2\right]^2 \frac{8J_s(s)J_s'(s)}{3s}\left\{\left[K_1\left(\frac{s\omega\rho}{v}\right)\right]^2 + \left[K_0\left(\frac{s\omega\rho}{v}\right)\right]^2\right\} \tag{172}$$

and the contribution to the cross section from impact parameters $\geq \rho_1$ is[29]

$$\sigma_{nn'}(v,\rho_1) = \left(\frac{2Z_p}{Z_c}\frac{n}{v}\right)^2\left\{\frac{4\pi}{3}\frac{J_s(s)J_s'(s)}{s^3}\right\}\frac{\rho_1 s}{v}K_0\left(\frac{s\rho_1}{v}\right)K_1\left(\frac{s\rho_1}{v}\right) \tag{173}$$

The probability (172) is valid for ρ much larger than that associated with unit $P_{nn'}$, which is obtained for small $\omega\rho/v \ll 1$, the sudden limit, when[29]

$$(v/v_n)(\rho/a_n) = n(Z_p/Z_c) \tag{174}$$

where a_n is the radius of the Rydberg orbital. Perturbation weak-coupling methods can therefore be taken as applicable in the region to the right of the inverse curve (174) in (ρ, v) space. To the left of (174), the effectively exact equivalent oscillator result (EOT), Eq. (169), must be used.

The line

$$(s\hbar\omega)(\tau_c/\hbar) \equiv s\omega_p/v \equiv (\rho/a_n)(sv_n/v) = 1 \tag{175}$$

in (ρ, v) space separates the sudden and adiabatic regions, which lie, respectively, above and below the diagonal (175). Sudden collisions, $\rho s v_n/a_n v \ll 1$, involve small ρ, large v, and, from (118) and (119), large energy transfers, whereas adiabatic collisions, $\rho s v_n/a_n v \gg 1$, involve large ρ, small v, and vanishingly small energy changes often less than the energy separation between adjacent levels (the classical inaccessible region). The probability of an adiabatic transition is usually small in comparison to that of a sudden transition such that the chief contribution to $\sigma_{nn'}$ arises from "sudden" impact parameters $\rho \ll \rho_S/s\omega$.

Weak coupling approximations to (169) are essentially valid for all $\rho \gtrsim a_n$ at relative speeds v and impact energies E_i, which satisfy[12]

$$v > v_A = (nv_n)(Z_p/Z_c), \qquad E_i > Z_c^2 R_1 \tag{176}$$

where R_1 is the Rydberg unit of energy, and are independent of the binding energy of the Rydberg electron. For lower impact speeds and energies in the ranges

$$v_A > v > v_B = (snZ_p/Z_c)^{1/2}, \qquad Z_c^2 R_1 > E_i > (2sZ_cZ_p/n)R_1 \tag{177}$$

where v_B is the intersection of (174) and (175), the sudden approximation (145) to (169) is valid for small ρ and the weak-coupling approximation (144)

to (169) for large ρ. The full EOT (169) is valid for all ρ. For lower speeds and energies in the range

$$v_n \ll v \lesssim v_B, \qquad 4I_n \lesssim E_i \lesssim (2sZ_cZ_p/n)R_1 \tag{178}$$

where I_n is the binding energy of the Rydberg electron with orbital speed v_n, the adiabatic region is extended down to much smaller ρ and the sudden region becomes contracted. Here EOT or, better still, the multichannel eikonal treatment MET (43) with (143) for the transition amplitudes in (44) and (45) is valid over all ρ.

At yet lower speeds $v \simeq v_n$, there is, in this section, no satisfactory perturbation-based treatment for transitions between close levels with $s \ll n$ in charged-particle–Rydberg collisions. The fixed two-centered scattering analysis[9] outlined in Sect. 11.2b is valid under the sole condition that

$$k_i = k_f + \frac{2\mu}{\hbar^2}\frac{(\epsilon_f - \epsilon_i)}{(k_i + k_f)} \simeq k_f\left[1 + \frac{s\omega}{k_f\bar{v}}\right] \simeq k_f \tag{179}$$

where $\bar{v}$ is some averaged projectile speed. This condition is satisfied provided $k_f\bar{v} \gg s\omega$, i.e., when the impact energy is much greater than the transition-energy $s\hbar\omega$. For ionization and excitational processes involving large changes in principle quantum number, none of the methods in this section based on the Heisenberg correspondence principle are satisfactory. Classical procedures, e.g., the Monte Carlo method of Abrines and Percival[10] and Abrines et al.[10] based on the solution of the equation of motion for the three-body system are applicable. For neutral collisions with Rydbergs, methods based on various simplifications of the analyses in Sects. 11.2b for scattering by a fixed two-centered Rydberg target, e.g., the impulse treatment, are applicable.

The previous correspondence methods - EOT and its sudden and weak-interaction limits - within MET (43) or its high-energy limit (53) are applicable to $nl \to n'l'$ collisional transitions in hydrogenic systems. Other Rydberg atoms exhibit an additional interesting feature, which is of special significance. In Na, for example, the energy splitting $\Delta\epsilon_l$ between successive lower-l levels associated with a given n correspond roughly to the energy separation between adjacent n levels. High-l levels become essentially indistinguishable because $\Delta\epsilon_l \simeq l^{-6}$. Thus the initial and final levels a and b in the transition $nl \to n'l'$ may well be embedded within clusters $c_{i,f}$ of levels. The energy separation of each cluster is approximately equal to the transition energy so that c_i and c_f may be regarded as being in resonance with a and b, respectively. Transitions within each cluster can be determined by the sudden approximation (145). The probability for $a \to c_i$ and $b \to c_f$ transitions is in effect unity for small-impact parameters $\rho \ll \rho_s$, the sudden limit ($v/s\omega$), such that the probability for $a \to b$ transitions can be satisfactorily determined by the first-order treatment (144). For intermediate $\rho \simeq \rho_s$, direct $a \to b$ transitions and $a \to c_{i,f}$ transitions are strongly coupled and compete. Transitions to $c_{i,f}$ may be regarded as loss mechanisms because the probability within a cluster of return-

ing from many l'' levels to a specified l' is relatively small. Percival and Richards[45] presented an interesting probability analysis of the situation and obtained an expression for the a → b transition probability in terms of the probabilities for the resonance transitions a → c_i, b → c_f and the first-order probability for a → b direct transitions. They illustrated their results by considering s → p collisional transitions, 10s → 10p(9d) and 11s(11p) → 12p(11d), where the resonant levels are enclosed in parentheses. The cross section for the first (single-resonance) collisional transition is greater at all electron-impact energies E than the latter (double-resonance) transition because the transition energy is smaller and the radial matrix element (123) in (172) is larger. Because of resonant depletion of the lower 11s state, the cross section for 11s → 12p transitions becomes markedly reduced at lower E, in contrast to that for the single-resonant (10s → 10p) case.

11.5. Quantal impulse and semiquantal methods

The quantal impulse approximation (QIA) was originally developed[46] by Chew, was extended by Chew and Wick and Chew and Goldberger for high-energy neutron scattering by deuterons, and has been derived from various directions.[23] The fixed-center analysis of Sect. 11.2b provides yet another new derivation of Eqs. (32) basic to QIA. However, the three basic assumptions underlying QIA of A–B(n) collisions become fully transparent from a derivation based on the exact two potential formula that are as follows:[2]

1. The interactions V_{12} and V_{32} of Rydberg electron 1 and projectile 3 with the B^+ core 2 are switched off during the 1–3 collision time and V_{12} is invoked only to establish the initial and final quantal states of $B(n)$.
2. The distortion of the motion of projectile 3 in the field V_{32} due to core 2 is neglected when interacting with both 2 and with 1.
3. Inelastic transitions in B are prohibited in direct A–B^+ encounters.
4. Although not essential to QIA, "on-the-energy-shell" 1–3 encounters are tacitly assumed, a procedure valid only in the high-energy or weak-binding limit.

These assumptions imply important considerations of special significance to A–B(n) collisions and will be discussed in Sect. 11.5b. Although conditions underlying the four items listed may be justified for A–B(n) direct collision processes at sufficiently high n and collision speeds $v_3 \gg v_1$ of the Rydberg electron, they may be seriously violated, particularly at thermal energies when $v_3 \ll v_1$.[2,47]

Flannery[1] derived, from classical-quantal principles, a *semiquantal* version of QIA suitable for A–B(n) ionizing collisions at high-impact energies, a version that was recently derived directly from QIA by replacing the final wave function $\phi_f(r)$ in (32) by a plane wave.[2] The analysis is sufficiently general so as to include a general (1–3) scattering amplitude $f_{13}(\mathbf{k}, \mathbf{k}')$ in contrast to the

other QIA derivatives (Sect. 11.5a and Chap. 8) that assume f_{13} either constant or a function only of the momentum change $\mathbf{P}=(\mathbf{k}'-\mathbf{k})$, as in Born's approximation.

Rydberg collisions at thermal energies involve, in addition to e–A encounters, a contribution from direct A–B^+ encounters.[2,47] Theory[2] of this nuclear-recoil effect may not only be applicable to l-changing and other quasi-elastic–elastic processes but may complement expressions for the shift and shape of spectral lines originating from highly excited levels $B(n)$ collision broadened by neutral perturbers A. This shift was predicted by Fermi[48] on the basis of S-wave scattering in slow e–A collisions and was generalized within the framework of QIA by Alekseev and Sobel'man[49] who also assumed that e–A collisions alone were responsible.

The quantal impulse treatment, its derivatives, and the validity criteria (which are easily violated[47] by several recent models for A–B(n) collisions) are discussed more fully by Flannery,[2] to which the reader is referred.

11.5a. Basic formulae in impulse treatments

From the basic QIA transition matrix element (32), the integral cross section for scattering of projectile 3 by the bound (1, 2) Rydberg system in the center of mass of the 3–(1, 2) system of reduced mass M_{AB} is

$$\sigma_{if}(k_3) = \left(\frac{M_{AB}}{M_{13}}\right)^2 \frac{k_3'}{k_3} \int |\langle g_f(\mathbf{k}_1 + \mathbf{P}) | f_{13}(\mathbf{k}, \mathbf{k}') | g_i(\mathbf{k}_1) \rangle_{\mathbf{k}_1}|^2 d\hat{\mathbf{k}}_3' \tag{180}$$

where $\mathbf{P}$ is the momentum change (32c) suffered in the (1–3) collision characterized by

$$f_{13}(\mathbf{k}, \mathbf{k}') = \frac{1}{4\pi}\left(\frac{2M_{13}}{\hbar^2}\right) T_{13}(\mathbf{k}, \mathbf{k}'); \qquad \mathbf{k}^{(\prime)} = \frac{M_3}{M}\,\mathbf{k}_1^{(\prime)} + \frac{M_1}{M}\,\mathbf{k}_3^{(\prime)} \tag{181}$$

the (on-and-off-the-energy-shell) amplitude for $\mathbf{k} \rightarrow \mathbf{k}'$ scattering of 1 and 3 in the center of mass of the (1–3) system with reduced mass M_{13} and by the conservation of momentum $\mathbf{k}_1 + \mathbf{k}_3$. At high energy $k_3 \simeq k_3'$ such that (180), with the aid of closure, yields the total elastic and inelastic cross section arising from (1–3) collisions as[2]

$$\sigma_{tot}(k_3) = (M_{AB}/M_{13})^2 \int |g_i(\mathbf{k}_1)|^2 |f_{13}(\mathbf{k}, \mathbf{k}')|^2 d\mathbf{k}_1\, d\hat{\mathbf{k}}_3' \tag{182}$$

When distortion in the scattering of 3 by the core C is neglected in the incident wave, which is then plane, the only contribution from (3–C) collisions is elastic and is given by Born's approximation. When the final state f in (180) is described by a plane wave, it can then be shown that the total cross section for all elastic and inelastic events arising from (1–3) collisions satisfies[47]

$$\sigma_{tot}(k_3) = (1/v_3) \int |g_i(\mathbf{k}_1)|^2 [v_{13}\sigma_{13}^{T}(v_{13})]\, d\mathbf{k}_1 \tag{183}$$

where σ_{13}^{T} is the total cross section for (1-3) scattering at relative speed v_{13} and v_3 the speed of the incident atom A. Cross section (183) is an upper limit to any collision process satisfying specific criteria (Sect. 11.5b) for validity of the e-A impulse approximation and shows that the rate $v_3\sigma_{tot}$ for all A-B(n) elastic and inelastic processes is limited by the total rate of free Rydberg e-A collisions with free momentum amplitude $g_i(\mathbf{k}_1)$ specified by the initial state of $B(n)$.

Plane-wave final state

When the final state of the Rydberg electron is described by a plane wave

$$\sigma_f(\mathbf{r}_1) = (2\pi)^{-3/2}\exp(i\boldsymbol{\kappa}_1'\cdot\mathbf{r}_1); \qquad g_f(\mathbf{k}_1') = \delta(\mathbf{k}_1' - \boldsymbol{\kappa}_1') \tag{184}$$

then the differential cross section for scattering into unit solid angle $d\hat{\mathbf{k}}_3'$ and for the final momentum of Rydberg electron to be within an interval $d\mathbf{k}_1'$ about $\mathbf{k}_1'$ is, with the aid of (180),

$$\left[\frac{d\sigma_{if}}{d\hat{\mathbf{k}}_3'\,d\mathbf{k}_1'}\right] = \left(\frac{M_{AB}}{M_{13}}\right)^2 \frac{k_3'}{k_3}|g_i(\mathbf{k}_1)|^2|f_{13}(\mathbf{k},\mathbf{k}')|^2 \tag{185}$$

which, in addition to the impulse requirement, assumes that the core is acknowledged only in the preparation of the initial state i and is "switched off" thereafter. It is this quantal result that yields[2] the semiquantal treatment previously developed[1] from a classical-quantal basis, which specified the cross section per unit of energy-change interval $d\epsilon$ about

$$\epsilon = (k_1'^2 - k_1^2)/2m_1 \tag{186}$$

per unit momentum-change interval dP about P, and per unit initial momentum interval $d\mathbf{k}_1$ about $\mathbf{k}_1(k_1, \theta, \phi_1)$. The polar angle θ_1 of $\mathbf{k}_1$ relative to $\hat{\mathbf{k}}_3$ along the Z axis can be expressed in terms of the momentum k of relative motion and of k_1 and k_3. Thus (185), in terms of these "classical" variables $(\epsilon, P, \mathbf{k}_1)$ rather than the set $[\hat{\mathbf{k}}_3'(\cos\theta_3', \phi_3'), \mathbf{k}_1', \theta_1', \phi_1')]$ natural to full quantal treatments, is

$$\frac{d\sigma_{if}}{(d\epsilon\, dP\, dk_1\, dk\, d\phi_1)} = \frac{k_1'^2}{J_{55}}\left(\frac{k_3'}{k_3}\right)\left(\frac{M_{AB}}{M_{13}}\right)^2 |g_i(\mathbf{k}_1)|^2|f_{13}(\mathbf{k},\mathbf{k}')|^2 \tag{187}$$

where the Jacobian of the five-dimensional transformation is[2]

$$J_{55} \equiv \frac{\partial(P, \epsilon, k_1, k, \phi_1)}{\partial(\cos\theta_3', \phi_3', k_1', \cos\theta_1', \phi_1')}$$

$$= \frac{M_3}{(M_1 + M_3)^2}\,\frac{k_1'^3(k_3k_3')^2}{k_1 kP}\,\sin\theta_1'\sin\theta_3'\sin(\phi_1' - \phi_3') \tag{188}$$

With the aid of conservation of momentum and energy, (187) with (188) eventually yields the semiquantal integral cross section[2]

$$\sigma_{SQ}(v_3) = \frac{1}{M_{13}^2 v_3^2} \int_{\epsilon_1}^{\epsilon_2} d\epsilon \int_{v_{10}}^{\infty} \frac{F_{nl}(v_1)\, dv_1}{v_1} \int_{P^-}^{P^+} dP \int_{g_-}^{g_+} \frac{|f_{13}(P, g)|^2\, dg^2}{[(g_+^2 - g^2)(g^2 - g_-^2)]^{1/2}} \tag{189}$$

where $g_\pm(P, v_1, \epsilon; v_3)$ and $P^\pm(v_1, \epsilon; v_3)$ denote limits to the relative (1-3) speed g and momentum change P consistent with fixed (P, v_1, ϵ) and (v_1, ϵ), respectively, where $\frac{1}{2}M_1[1 + (M_1/M_2)]v_{10}^2$ is $\max(0, \epsilon)$ and $\epsilon_{1,2}$ the limits to ϵ. The initial distribution in speed v_1 of the Rydberg electron in state nl is

$$F_{nl}(v_1)\, dv_1 = \frac{2}{2l+1} \left(\int \sum_{m=-l}^{l} |g_{nlm}(\mathbf{k}_1)|^2\, d\phi_1 \right) k_1^2\, dk_1 \tag{190}$$

which can be determined from the initial wave function $\phi_{nlm}(\mathbf{r})$. In situations where the (1-3) scattering amplitude $f_{13}(\mathbf{k}, \mathbf{k}')$ is expressed as $f_{13}(g, \psi)$, where ψ is the scattering angle, then (189) can be rewritten alternatively as[1]

$$\sigma_{SQ}(v_3) = \frac{1}{v_3^2} \int_{\epsilon_1}^{\epsilon_2} d\epsilon \int_{v_{10}}^{\infty} \frac{F_{nl}(v_1)\, dv_1}{v_1} \int_{g_-}^{g_+} \frac{g\, dg}{S(v_1, g; v_3)} \times \int_{\psi^-}^{\psi^+} \frac{|f_{13}(g, \psi)|^2\, d(\cos\psi)}{[(\cos\psi^+ - \cos\psi)(\cos\psi - \cos\psi^-)]^{1/2}} \tag{191}$$

where $\psi^\pm(g, v_1, \epsilon; v_3)$ are certain angular limits[1,2] to the scattering and ensure a given energy change ϵ for fixed g, v_1, and v_3 and where S is also a known function.[1,2] Cross sections are more efficiently calculated from the semiquantal formula (189) or (191) than from their quantal equivalent (185), which gives

$$\sigma_{if} = \left(\frac{M_{AB}}{M_{13}} \right)^2 \frac{k_3'}{k_3} \int |g_i(\mathbf{k}_1)|^2 |f_{13}(\mathbf{k}, \mathbf{k}')|^2\, d\mathbf{k}_1'\, d\hat{\mathbf{k}}_3' \tag{192}$$

for the integral cross section.

When f_{13} is taken as the Born amplitude, then the SQ treatment for

$$\mathrm{H(1s)} + \mathrm{H(1s)} \rightarrow \begin{cases} \mathrm{H}(n) \\ \mathrm{H}(\Sigma) \end{cases} + \mathrm{H}^+ + e \tag{193}$$

at high-impact energies reproduces[1] the quantal Born results of Omidvar and Kyle.[50] Semiquantal methods have also been applied to[51]

$$\mathrm{H(1s)} + \mathrm{H(1s)} \rightarrow \begin{cases} \mathrm{H(1s)} + \mathrm{H}^+ + e \\ \mathrm{H}(1,2) + \mathrm{H}(n') \end{cases} \tag{194}$$

with successful results and to[52]

$$\mathrm{H}(nl) + \mathrm{H}(n_0 l_0) \rightarrow \mathrm{H}(n'l') + \mathrm{H}^+ + e \tag{195}$$

where the interesting systematic trends discussed in Sect. 11.2d were exhibited. We recall that any treatment, such as SQ, based on QIA is valid only when momentum and energy changes imparted in e-A collisions are greater than any momentum and energy imparted to e by its core during the collision (see Sect. 11.5b).

Further approximations will follow from (180) upon the use of closure or the peaking approximation.

$f_{13}(\mathbf{P})$

In particular, when f_{13} in (180) or implicitly in (32) is a function *only* of momentum change $\mathbf{P}=(\mathbf{k}'-\mathbf{k})$, then

$$T_{fi}(\mathbf{k}_3,\mathbf{k}_3') = T_{13}(\mathbf{P})F_{fi}(\mathbf{P}) \tag{196}$$

such that when the free (1–3) scattering is described by the Born approximation, then

$$T_{fi}^{(\mathrm{B})}(\mathbf{k}_3,\mathbf{k}_3') = T_{13}^{(\mathrm{B})}(\mathbf{P})F_{fi}(\mathbf{P}) \tag{197}$$

which is simply the Born result (22) for A–B(n) collisions. This is the form of QIA exploited extensively by Matsuzawa (see Chap. 8) and used by Matsuzawa[53] in situations where it may not describe the actual state of affairs either in validity or in mechanism.[47]

The full impulse expression (180) and its semiquantal derivatives (185), (189), or (191), which are all equivalent, provide, via a general $f_{13}(\mathbf{k},\mathbf{k}')$, a scattering description much more general than (193), which is valid only at high-impact energies. Moreover, the semiquantal cross section for all elastic and inelastic events yields a result identical with (183) given by the full QIA.

$f_{13}=A$

When f_{13} can be taken as a constant scattering length A, then

$$\sigma_{if}(\mathbf{k}_3) = \frac{2\pi A^2}{k_3^2}\left(\frac{M_{\mathrm{AB}}}{M_{13}}\right)^2 \int_{(k_3-k_3')}^{(k_3+k_3')} |F_{fi}(\mathbf{P})|^2 P\,dP \tag{198}$$

such that (183) for the total cross section gives

$$\sigma_{\mathrm{tot}}(k_3) = \frac{4\pi A^2}{v_3}\int v_{13}|g_i(\mathbf{k}_1)|^2\,d\mathbf{k}_1 \rightarrow \begin{cases} 4\pi A^2, & v_3 \gg v_1 \quad (199a) \\ \dfrac{\langle v_1\rangle}{v_3}\,4\pi A^2, & v_3 \ll v_1 \quad (199b) \end{cases}$$

where $\langle v_1\rangle$ is the mean speed of the Rydberg electron. However, at high v_3, T_{13} is never constant so that (199a) is never attained in practice, whereas at low v_3, (199b) must be augmented by contributions from direct collision with the Rydberg core. Note that $v_3 \ll v_1$ for principal quantum numbers[2]

$$n \ll 870 M_{\mathrm{AB}}^{1/2}(300/T)^{1/2} \tag{200}$$

where the reduced mass is in atomic mass units and where T is the temperature such that (200) is satisfied in most cases of interest for thermal atoms A. The total cross section (113) for this case is then

$$\sigma_{\text{tot}}^{13}(v_3) = \frac{1}{v_3}\int |g_i(\mathbf{k}_1)|^2 v_1 \sigma_{13}^{\text{T}}(v_1)\, dv_1$$

$$\equiv \frac{1}{v_3}\langle v_1 \sigma_{13}^{\text{T}}(v_1)\rangle; \qquad v_1 \gg v_3 \tag{201}$$

the average rate for e–A collisions divided by the projectile speed v_3, a rate that may be augmented by the contribution σ_{tot}^{23} from 2–3 collisions. The minimum temperatures T corresponding to $\frac{3}{2}kT$ energy of relative motion required for $n \rightarrow n+s$ excitation and ionization of H(n) are

$$T_{\text{E}}(K) = (10/n)^3 300\text{s} \tag{202a}$$

$$T_{\text{I}}(K) = (23/n)^2 300 \tag{202b}$$

respectively.

11.5b. Validity criteria

Rigorous criteria for validity of QIA of A–B(n) collisions have been properly traced via a derivation of QIA from the exact two-potential formula.[2] The assumptions basic to QIA imply the following conditions for A–B(n) collisions.[47]

Condition A

Switching off the core interactions $V_{12}+V_{32}$ during the (1–3) collision time τ_c implies that energy can be controlled only to within imprecision $\Delta E_1 \simeq \hbar/\tau_c$ during the collision, i.e., $\sigma_{13}(v_{13})$ must not exhibit too rapid a variation with v_{13} such as would occur, e.g., in the neighborhood of either an A^- resonance or a Ramsauer minimum evident for e–Ar, Kr, and Xe scattering. This implication has been ignored in several studies (as in Matsuzawa[53] and Hickman[54]). When $v_1 \gg v_3$, $\tau_c \simeq A_1 n$ (a.u.), where $A_1(a_0)$ is the e–A interaction distance such that, during τ_c, $\Delta E_1 \simeq (A_1 n)^{-1}$ a.u. is comparable with the small impact energy $\frac{1}{2}v_1^2$. For $v_3 \gg v_1$, $\Delta E_1 \simeq v_3/A_1$, which is much less than $\frac{1}{2}v_3^2$ the relative energy over which σ_{13}, in general, varies slowly.

Condition B

The momentum P transferred (impulsively) to 1 during τ_c must be much greater than the momentum imparted to 1 during τ_c via the force F associated with core interaction V_{12}, i.e.,

$$P \gg \int_{\tau_c} F\,dt = |\langle \phi_{nl}|-\nabla V_{12}|\phi_{nl}\rangle|\tau_c \simeq \tau_c/n^3(l+\tfrac{1}{2}) \tag{203a}$$

such that in terms of the orbital period T_n,

$$\tau_c \ll T_n(l+\tfrac{1}{2})P, \qquad T_n \simeq n^{-3} \text{ (a.u.)} \tag{203b}$$

If V_{12} varies sufficiently slowly (but need not be necessarily small!) over the range A_1 of the collision interaction V_{13} such that the force F ($\equiv -\nabla V_{12}$) due to the core is small in comparison with the force ($-\nabla V_{13}$) due to the Rydberg electron–projectile interaction, then (203) is satisfied; in this sense, V_{12} can be regarded as "quasi-classical."

For ionizing collisions, $P \gtrsim n^{-1}$, then $\tau_c \ll T_n$ for circular orbits ($l \simeq n$) and $\tau_c \ll T_n/n$ for highly eccentric orbits ($l \simeq 0$). Hence $\tau_c \ll n^{-2}$ covers electron ejection from all orbits. For nonionizing collisions, P [Eq. (203)] cannot become arbitrarily small, which could occur for quasi-elastic or l-changing collisions. At thermal energies, $v_1 \simeq n^{-1}$, which is greater than $v_3 \simeq 10^{-4}$ a.u. for most n of interest, and $\tau_c \simeq A_1 n$ such that (203) implies that $P \gg A_1/n^2(l+\frac{1}{2})$. The angular momentum change ΔL for n fixed due to e–A implusive encounters at distance R_{12} from B^+ must therefore satisfy

$$\Delta L \simeq P\langle R_{12}\rangle \simeq \tfrac{1}{2}P[3n^2 - l(l+1)] \gg \tfrac{1}{2}A_1[3n^2 - l(l+1)]/n^2(l+\tfrac{1}{2}) \tag{204}$$

which is, in general, fulfilled only at the highest initial l when the permitted $\Delta L \gg A_1/l$. Small initial l require from (204) large changes $\Delta L \gg A_1$ for impulse model validity (because then the momentum imparted by the core on the highly elliptical orbits becomes considerably strengthened over that for circular orbits). Detailed discussion on the implication of (203a) to angular momentum changes is given in Ref. 47 (second listing).

Condition C

Cross section (183) is an upper bound for any process based on e–A encounters and described by QIA, SQ, or any derivative of QIA. Thus,

$$\sigma_{\text{tot}}^{(13)}(v_3) = \begin{cases} \langle v_1 \sigma_{13}^{\text{T}}(v_1)\rangle / v_3, & v_1 \gg v_3 \quad \text{(205a)} \\ \sigma_{13}^{\text{T}}(v_3), & v_1 \ll v_3 \quad \text{(205b)} \end{cases}$$

Condition D

The second assumption listed at the beginning of this section implies that 1 and 2 behave as separate and as independent scatterers. This is valid provided that $R_{12} \simeq n^2 a_0 \ll A_{1,2}$ the scattering amplitudes for (1–3) and (2–3) collisions and that the reduced wavelength $\lambda\!\!\!^{-}_{i3}$ for (i–3) relative motion is much less than R_{12} so that A_1 is not affected by A_2 and vice versa. In general, $\lambda\!\!\!^{-}_{13} \ll n^2$ at all energies even for $v_1 \ll v_3$, when $\lambda\!\!\!^{-}_{13} \simeq n$. Also, for (2–3) collisions at thermal energy, $\lambda\!\!\!^{-}_{23} \simeq k_3^{-1} \simeq 10^{-1}$. Hence, $R_{12}^2 \gg \lambda\!\!\!^{-}_{i3} A_i$ such that multiple scattering can be neglected. This condition is the one most easily and generally satisfied in Rydberg collisions, but it alone is not sufficient for QIA validity.

Condition E

Distortion of motion of 3 when interacting with 1 due to core 2 can, in general, be neglected except at thermal energies when the cross section for (2-3) encounters are large ($\sim 10^3$ Å^2). Impulse expression (32) must then be appropriately generalized. The result involves a nine-dimensional integral for the T matrix.[2]

Condition F

Quantal impulse approximation and its derivatives are based on (1-3) encounters whether or not they are distorted by V_{32} and contain no inelastic transitions that can arise in direct (2-3) encounters. Hahn[56] recently showed that the distortion correction to l-changing collisions owing to the 2-3 interaction is large for intermediate values of $n \lesssim 20$ and that the effect on the T matrix for 2-3 collisions through higher-order terms neglected in the customary impulse approximation can be very important. Lane and Preston[57] demonstrated via a direct numerical Monte Carlo classical simulation that the core is very important in the ionization of Rydberg atoms (Ar(ns), $n \gtrsim 30$) by thermal dipole molecules (as HCl).

11.5c. Binary encounter methods for charged-particle–Rydberg collisions

When $|f_{13}|^2$ in (191) is replaced by $(4\hbar^4 Z^2/P^4 a_0^2)$, the differential cross section for on-the-energy-shell Coulomb scattering of the Rydberg electron 1 by an incident ion (or electron) of charge Ze, then the differential cross section for energy change ϵ reduces, for given initial speeds v_1 and v_3, to

$$\frac{d\sigma}{d\epsilon}(v_1, v_3) = \frac{4\pi Z^2 e^4}{3 v_1 v_3^2} [P_\ell^{-3} - P_u^{-3}] \tag{206}$$

The momentum-change limits,

$$\begin{aligned} P_u &= \min[p_1^+ = M_1(v_1 + v_1'), p_3^+ = M_{AB}(v_3 + v_3')] \\ P_\ell &= \max[p_1^- = M_1|v_1' - v_1|, p_3^- = M_{AB}|v_3 - v_3'|] \end{aligned} \tag{207}$$

are (p_1^-, p_1^+), (p_3^-, p_1^+), and (p_3^-, p_3^+), provided ϵ $(\gtrsim 0)$ is, respectively, within limits $[0, \epsilon^-]$, $[\epsilon^-, \epsilon^+]$, and $[\epsilon^+, \frac{1}{2} M_{AB} v_3^2]$, where

$$\epsilon^\pm = \frac{4 M_1 M_3}{(M_1 + M_3)^2} [\tfrac{1}{2} M_{AB} v_3^2 - \tfrac{1}{2} M_1 v_1^2 \pm \tfrac{1}{2}(M_3 - M_1) v_1 v_3] \tag{208}$$

are the kinetic energies transferred from 3 to 1, which is initially moving with speed v_1 directed, respectively, toward or away from 3. The energy range $\epsilon > \epsilon^+$ is entered provided $p_3^+ < p_1^+$, i.e., provided

$$2M_1 v_1 - v_3(M_3 - M_1) > 0 \tag{209}$$

which ensures real final speeds v_1' and v_3'. Hence,

$$\frac{d\sigma}{d\epsilon}(v_1, v_3) = \frac{4\pi Z^2 e^4}{3 v_1 v_3^2 \epsilon^3} I(\epsilon; v_1) \tag{210}$$

where

$$I(\epsilon; v_1) = v_1\left(v_1^2 + \frac{3\epsilon}{2M_1}\right), \qquad 0 \leqslant \epsilon \leqslant \epsilon^- \tag{211a}$$

$$= \left[v_3 + \left(v_3^2 - \frac{2\epsilon}{M_{AB}}\right)^{1/2}\right]^3 - \left[\left(v_1^2 + \frac{2\epsilon}{M_1}\right)^{1/2} - v_1\right]^3 \equiv (v_3 + v_3')^3 - (v_1' - v_1)^3, \qquad \epsilon^- \leqslant \epsilon \leqslant \epsilon^+ \tag{211b}$$

$$= \left(v_3^2 - \frac{2\epsilon}{M_{AB}}\right)^{1/2}\left(v_3^2 - \frac{\epsilon}{2M_{AB}}\right) \equiv v_3'\left(v_3'^2 + \frac{3\epsilon}{2M_{AB}}\right), \qquad \epsilon^+ \leqslant \epsilon \leqslant \tfrac{1}{2} M_{AB} v_3^2 \tag{211c}$$

which is zero for $\epsilon \geqslant \epsilon_{max} = \frac{1}{2} M_{AB} v_3^2$, the maximum energy that can be transferred.

For incident electrons, $\epsilon^+ = \epsilon^-$, and I is given by (211a) or (211c), where appropriate. For incident ions, only (211a) and (211b) are appropriate because (209) is never satisfied for $v_3 > v_1$. On integrating over the symmetrical velocity distribution $F_{nl}(v_1)$ appropriate to Rydberg state nl, the binary-encounter cross section for ionization by a charged particle is

$$\sigma_{nl}(v_3) = \frac{4\pi Z^2 e^4}{3 v_3^2} \int_{I_n}^{\epsilon_{max}} \epsilon^{-3}\, d\epsilon \int_0^\infty v_1^{-1} F_{nl}(v_1) I(\epsilon; v_1)\, dv_1 \tag{212}$$

where I_n is the binding energy. For sufficiently high n, when $\frac{1}{2} M_1 v_1^2$ can be replaced via the Virial theorem by I_n, then, for incident electrons, $(M_3 = M_1)$,

$$\frac{d\sigma_e^{(e)}}{d\epsilon} = \frac{\pi e^4}{\frac{1}{2} M_1 v_3^2}\left(\frac{1}{\epsilon^2} + \frac{4}{3}\frac{I_n}{\epsilon^3}\right), \qquad 0 < \epsilon \leqslant \epsilon^{\pm} = \frac{1}{2} M_{AB} v_3^2 - I_n \tag{213}$$

which is the main contribution and

$$\frac{d\sigma_e^{(e)}}{d\epsilon} = \frac{\pi e^4}{\frac{1}{2} M_{AB} v_3^2}\left(\frac{v_3'}{v_1}\right)\left(\frac{1}{\epsilon^2} + \frac{2M_{AB} v_3'^2}{3\epsilon^3}\right), \qquad \epsilon^{\pm} < \epsilon \leqslant \frac{1}{2} M_{AB} v_3^2 \tag{214}$$

which is negligible, being operative only over the small end range I_n of energy change. Hence, for collisional ionization by electrons of energy E,

$$\sigma_1^{(e)}(E) = \frac{\pi e^4}{E/I_n}\left[\frac{5}{3}\frac{1}{I_n^2} - \frac{(E/I_n) - \frac{1}{3}}{[(E/I_n) - 1]^2}\right] \simeq \frac{An^4}{E/I_n} + \frac{B}{(E/I_n)^2} \tag{215}$$

which exhibits an n^4 dependence for asymptotic impact energies E *measured in units of the binding energy* I_n, where A and B are constants. Cross sections for ion impact can be similarly obtained from (211).

Although the binary-encounter formulae were derived here from the semiquantal treatment (Sect. 11.5a) for a general scattering amplitude $f_{13}(g, \psi)$ and (1-3) interaction, similar or identical expressions have been derived by more direct means[58,59] for Coulomb interactions alone, or when f_{13} is a function only of momentum change P, and have received widespread application and review[58] in atomic collision physics. They can be generalized to include electron exchange,[58] which is not important, however, for Rydberg collisions. Whereas the effect of the core on the orbital speed v_1 is acknowledged via (212), its effect (acceleration and focusing) in the projectile can be acknowledged (but not rigorously justified) by replacing the outside factor E^{-1} in (206), (212), and (215) by $E+\alpha$, where α is 3.25,[58,60] to agree with the classical three-body sections of Abrines et al.[10]

For e-metastable rare gas collisions, (212) yields[61] close agreement with experiment, with Born's approximation, and to within 10-20% of (215) with $\alpha = 3.25$.[60] Apart from their simplicity, the main attraction of the binary-encounter formulae for Rydberg collisions is that they automatically include an infinite summation over all angular momenta l_ϵ of the ejected electron. In e-excited atom collisions., many l_ϵ are required for converged $d\sigma/d\epsilon$,[61] and the contributions from high-order multipoles are substantial in comparison to the dipole contribution (a feature exhibited also in direct excitation (Sect. 11.2d) and consistent with the quasi-classical nature of the Rydberg electron). Direct application of even Born's approximation of ionization is, therefore, time-consuming, and the binary-encounter expressions (206)-(215) for charged-particle impact or the more general semiquantal (SQ) formulae (189) or (191) for neutral impact represent very efficient methods for calculation of cross sections σ_1 for ionization of Rydberg atoms. For neutral impact, SQ yields $\sigma_1 \simeq E^{-1}$ in accord with the correct Born-Bethe asymptotic limit when no projectile excitation occurs, and when f_{13} for e-A collisions is replaced by the corresponding Born value, SQ reproduces the Born cross sections for A-B(n) ionizing collisions.

The binary-encounter cross section (206) and the classical three-body cross section[10] for charged-particle collisions yield the incorrect E^{-1} asymptotic energy dependence in contrast to the correct Born-Bethe asymptote $E^{-1}(A \ln E + B)$. For excitation and ionization from excited states, the dipole contribution A is very small in comparison to B (even for e-He($2\,^{1,3}$S) collisions; see fifth listing in Ref. 8 and Refs. 19 and 61), so that $A \ln E$ becomes effective only at extremely high energies ($\gtrsim$1000 eV for e-He($2\,^3$S) collisions;

see Fig. 11.1) and the validity of the binary encounter result (206) is extended to much higher-impact energies.

11.5d. Extension of binary-encounter method to asymptotic energies

The binary-encounter (BE) method is applicable only when the collision time $\tau_c \simeq \rho/v \ll T_n$, the orbital period, a criteria that becomes invalid for distant encounters ρ, which are, therefore, not properly treated by BE so that, for asymptotic charged-particle collisions, the $\ln E$ dipole term, which originates from distant encounters, is absent in BE. This inadequacy of BE in its omission of adiabatic effects can be remedied either by using the Fourier components of the energy change ϵ in accord with proper correspondence arguments, as pointed out by Percival and Richards,[38] or, alternatively, as presented here, by invoking the Weizsäcker–Williams principle of virtual quanta.[37]

Here the electrostatic field of a passing charged particle at high energies is replaced by that arising from an equivalent flux of photons, which also involves a (negligible) magnetic interaction. For distant encounters, with $\rho \geqslant \rho_{\min}$,

$$d\sigma/d\epsilon = N(\hbar\omega)\sigma_1(\hbar\omega), \qquad \epsilon = \hbar\omega, \quad \rho \geqslant \rho_{\min} \tag{216}$$

where $N\,d\epsilon$ is the number of virtual photons in the equivalent photon field and σ_1 the cross section for photoejection of the Rydberg electron of mass M_1 by a photon of energy ϵ. For a straight-line incident path, then[37]

$$N(\hbar\omega) = \frac{2}{\pi}\frac{Z^2e^2}{\hbar c}\left(\frac{c}{v_3}\right)^2\frac{1}{\epsilon}\left\{\chi K_0(\chi)K_1(\chi) - \frac{v_3^2}{2c^2}\chi^2[K_1^2(\chi) - K_0^2(\chi)]\right\} \tag{217}$$

where K_i are modified Bessel functions of argument

$$\chi = \frac{\omega\rho_{\min}}{v_3} = \frac{(\epsilon\beta)n^2a_0}{\hbar v_3} \equiv \left(\frac{I_1}{\frac{1}{2}M_1v_3^2}\right)^{1/2}\left(\frac{\beta\epsilon}{2I_n}\right) \tag{218}$$

in which $\rho_{\min}$ is taken as β times the Rydberg radius n^2a_0. Hence, for photon energies $\hbar\omega \geq (1/n^2)(e^2/a_0)$, which contribute most to the integral cross section, $\chi \ll 1$, with the result that

$$N(\hbar\omega) = \frac{2}{\pi}\left(\frac{Z^2e^2}{\hbar c}\right)\left(\frac{c}{v_3}\right)^2\frac{1}{\hbar\omega}\left[\ln\left(\frac{1.123}{\chi}\right) - \frac{v^2}{2c^2}\right] \tag{219}$$

The photoejection cross section in terms of the differential oscillator strength (126) and binding energy I_n is

$$\sigma_1 = 2\pi^2\alpha a_0^2\,(df/d\epsilon_{\text{au}}) \simeq 4\pi^2\alpha a_0^2 n(I_n/\epsilon)^3, \qquad \alpha = e^2/\hbar c \tag{220}$$

with the result that, for distant collisions,

$$\left(\frac{d\sigma}{d\epsilon}\right)_{\mathrm{D}} = \frac{4\pi Z^2 a_0^2}{\frac{1}{2}M_1 v_3^2}\left(\frac{I_n}{\epsilon}\right)^4 n^3 \ln\left[\frac{1.123^2}{\beta^2}\left(\frac{2M_1 v_3^2}{I_1}\right)\left(\frac{I_n}{\epsilon}\right)^2\right] \quad (221)$$

which includes the ln term of quantal treatments. Because $\epsilon \gtrsim I_n$, the argument of this term is inappreciable unless $\frac{1}{2}M_1 v_3^2 \gtrsim I_1 \gg I_n$, i.e., at extremely high energies. The classical energy change ϵ in a Coulombic binary encounter with impact parameter ϵ is

$$\epsilon(\rho) = \frac{(Ze^2)^2}{\frac{1}{2}M_1 v_3^2}(\rho^2 + \rho_{\min}^2)^{-1} \quad (222)$$

so that for close collisions,

$$\left(\frac{d\sigma}{d\epsilon}\right)_{\mathrm{C}} = 2\pi\rho\frac{d\rho}{d\epsilon} = \frac{\pi Z^2 e^4}{\frac{1}{2}M_1 v_3^2}\frac{1}{\epsilon^2} \equiv \frac{4\pi Z^2 a_0^2}{\frac{1}{2}M_1 v_3^2}\left(\frac{I_n}{\epsilon}\right)^2 n^4 \quad (223)$$

which agrees with the first term of (213) and which dominates (221) for high n and impact energy up to many I_n. The combination of (223) or of (206) in general, for close encounters with (221) for distant encounters yields the correct $A(1+B\ln E)/E$ dependence at high-impact energies.

A similar procedure for collisional $n \to n'$ transitions yields

$$\sigma_{nn'}(v_3) = N(\hbar\omega_{nn'})\sigma_{\mathrm{A}}(\hbar\omega_{nn'}) \equiv (2\pi^2\alpha a_0 e^2) f_{nn'} N(\epsilon_{nn'}) \quad (224)$$

where σ_{A} is the photoabsorption cross section, such that the aid of (123) and (124) for the oscillator strength and of (219),

$$\sigma_{nn'}(v_3) = \frac{4}{3}\frac{n^4\pi a_0^2}{(\frac{1}{2}M_1 v_3^2)}\left(\frac{e^2}{a_0}\right)\frac{1+(s/n)}{s^3} \times J_s(s)J_s'(s)g(s)\ln\left[\frac{1.123^2}{\beta^2}\left(\frac{2M_1 v_3^2}{I_1}\right)\left(\frac{I_n}{\epsilon_{nn'}}\right)^2\right] \quad (225)$$

The ln term is therefore negligible when both n and s are large compared with unity and the binary-encounter result (215) appropriately modified by taking $d\epsilon = (I_1/n'^3)$ provides the dominant contribution. The result (225) essentially agrees with Percival and Richards,[38] who derived it from consideration based on detailed balance and on Fourier components of ϵ.

11.6. Monte Carlo procedures

Monte Carlo simulations of three-body collisions have been performed for rates of collisional excitation of Rydbergs by thermal electrons[11] and for the cross sections of collisonal ionization of H(n) by high-energy monochromatic electrons and protons.[10] For thermal electrons in a plasma, only a small fraction of collisions contribute to direct excitation and ionization, and the overall distribution of excited atoms among their discrete and continuous states is

determined by the balance of upward and downward cascading. The energy transfers are small and the collisions are adiabatic in general. The procedure of Mansbach and Keck[11] focused on an equilbrium rate of collisional deexcitation $i \rightarrow f$, based on Monte Carlo simulation of the fraction of collisions causing deexcitation combined with a variational (or bottleneck) treatment of recombination[62] for the rate at which atoms cross some energy level S between i and f. In this sense, the method can be considered as complementary to that of Percival and associates[10] for direct excitation at much higher energies. These procedures were fully documented elsewhere.[10-12,62] It was noted by Vriens and Smeets[63] that the rates of Mansbach and Keck[11] are accurate only over a limited adiabatic range of electron temperatures; extrapolation to the sudden regime is without validity. (For more detail, Monte Carlo simulations of neutral-neutral collisions were described in Chap. 6).

11.7. Semiempirical electron-impact cross sections

In an effort to provide working formulae for cross sections over a wide range of impact energies without recourse to explicit application of the appropriate theoretical treatments in the previous sections, many authors have produced, to various degrees of compatibility, semiempirical fits based on available experimental and theoretical data and variations. The most recent semiempirical cross sections[60,63] for charged-particle impact should suffice until such time when implementation of the preceding detailed theories over relevant energy ranges becomes available, although the fits of Gee et al.[63] are based on the strong-coupling correspondence principle.

Based on the binary-encounter method of Sect. 11.5d, Vriens and Smeets[60] recommend

$$\sigma_n^{\mathrm{I}}(E) = \frac{\pi e^4}{(E + 3.25 I_n)} \left[\frac{5}{3 I_n} - \frac{1}{E} - \frac{2}{3} \frac{I_n}{E^2} \right] \tag{226}$$

as the cross section for collisional ionization of Rydberg atoms with ionization potential I_n by electrons of energy $E \gtrsim I_n$. This expression has the correct BE limit (215) at high E (the logarithmic term is negligible for excited states), reproduces the classical three-body Monte Carlo results (Sect. 11.6) to within statistical accuracy (10%) for all E, and agrees within 10 to 20% with the more elaborate binary encounter results of both Ton-That and Flannery[61] given by the full expression (212) for electron-impact ionization of metastable rare gases, which agree with available experiment, and of Roy and Rai[64] for ionization of ground-state alkali atoms.

The recommended cross section for $p \rightarrow q$ excitation by electron impact is[60]

$$\sigma_{pq}(E) = \frac{\pi a_0^2 (2R)}{E + (\alpha_{pq} R)} \left[A_{pq} \ln\left(\frac{E}{2R} + \beta_{pq} \right) + B_{pq} \right] \tag{227a}$$

where R is the Rydberg unit of energy (13.6 eV),

$$A_{pq} = (2R/E_{pq})f_{pq} \tag{227b}$$

in terms of the absorption oscillator strength f_{pq} for a transition of energy E_{pq}, and

$$B_{pq} = \frac{1}{p^3}\left(\frac{2R}{E_{pq}}\right)^2\left[1 + \frac{4}{3}\frac{I_p}{E_{pq}} + \frac{b_p}{p}\left(\frac{I_p}{E_{pq}}\right)^2\right] \tag{227c}$$

in terms of the ionization potential I_p and of b_p given as[60]

$$b_p = 1.41 \ln p - 0.7 - (0.51/p) + (1.16/p^2) - (0.55/p^3) \tag{227d}$$

In the absence of α_{pq} and β_{pq}, (227) provides the correct high-energy limit. A simple yet accurate expression for f_{pq} was given by Johnson[65] whose semiempirical cross sections are not as accurate as those just given. For $p - q \gtrsim p \gg 1$, then $B_{pq} \gg A_{pq}$, the last term in (227c) is negligible ($\ll 1$), and (227a) reduces to the correct binary-encounter limit, obtained for excitation by multiplying (213) by $2R/p^3$. Extrapolation to lower-impact energies E is provided by introducing in (227a) the parameters[63]

$$\beta_{pq} = \exp(-B_{pq}/A_{pq}) - (0.4E_{pq}/R) \tag{227e}$$

and

$$\alpha_{pq} = [8 + (23s^2/p^2)]/[8 + 1.1ps + (0.8/s^2) + 0.4(n^3/s)^{1/2}|s - 1|] \tag{227f}$$

which depend only on properties of the Rydberg atom.

The preceding expressions yield excitation cross sections that are finite at threshold, a feature correct for excitation[66] because of dipole coupling between degenerate levels. Cross sections for $q \to p$ deexcitation are obtained from (227) by the use of the detailed balance relation.

Figure 11.4 illustrates the semiempirical excitation cross sections (227) of Vriens and Smeets[60] for various $p \to q$ transitions in atomic hydrogen together with those of Gee et al.[63] The overall agreement is good only at the higher-impact energies $E > 4I_p$, where Gee et al. claim accurate results.[63]

11.8. Summary

In this chapter we presented a comprehensive and unified account of the theory of Rydberg collisions with electrons, ions, and neutrals. The methods given ranged from quantal to classical descriptions, with necessary emphasis on the semiclassical analysis of the motion of either the (internal) Rydberg electron or (external) incident projectile, or both. The internal semiclassical wave functions not only provided both Bohr–Sommerfeld quantization and the Heisenberg correspondence principle, two valuable and essential assets for Rydberg atoms, but also lent themselves quite naturally in the action-angle variable representation to perturbation treatments based on the Hamilton–Jacobi equation. The fixed-center quantal method (Sect. 11.2b) led directly

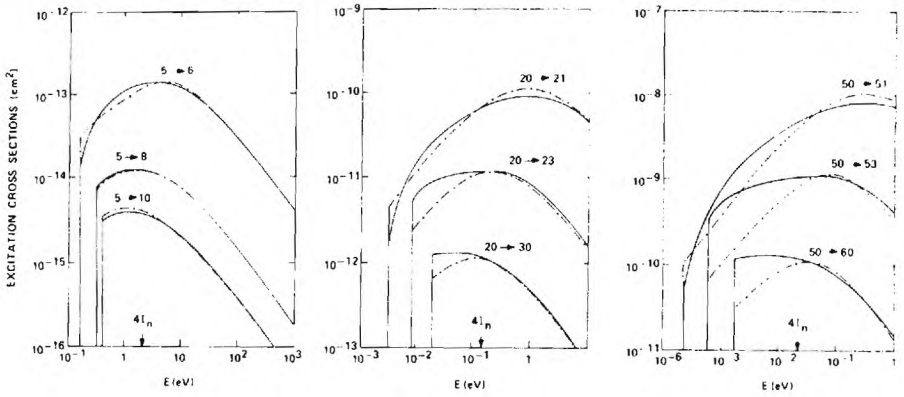

Fig. 11.4. Semiempirical cross sections[60] for $p \to n$ transitions in e–H(p) collisions for $p = 5$, 20, and 50, where I_n is the ionization energy for H(p). Solid curves: Eq. (227a) from Ref. 60; broken curves: from Ref. 63.

to the full quantal impulse treatment and to its semiquantal and binary-encounter derivatives (Sect. 11.5). It also can be used for rearrangement and charge-transfer-ion–atom collisions.[9] The methods were presented here with the aim of providing a basic theoretical foundation for many future detailed investigations of various processes involving Rydberg atoms.

Thermal collisions that simply mix a small number of angular momentum l states within a given n can be accurately described by quantal or semiclassical close-coupling procedures (Sects. 11.2a and 11.3a), the only methods, apart from impulse treatments, that originate from studies of ground-state collisions. In A–B(n) thermal collisions, the speed of the Rydberg electron remains much greater than the A–B^+ relative speed so that, in order to examine the effects of the core B^+, some suitable molecular treatment that provides the response of the Rydberg electron to the charging field of the AB^+ ionic complex is required. For nl–nl' transitions, the close-coupling formalism of Arthurs and Dalgarno[17] is directly applicable, whereas for $n \to n'$ thermal collisions, the approach of Janev and Mikalov[67] is interesting.

Collisional transitions between neighboring or adjacent Rydberg levels n and n' are best handled in terms of the equivalent oscillator theorem (Sect. 11.4d) or its sudden and weak-coupling limits, when appropriate, for determination of the transition amplitudes. These amplitudes can then be inserted into a properly constructed semiclassical analysis (Sect. 11.3) of the collision cross section, e.g., the multichannel eikonal treatment[8] (Sect. 11.3a) for electron impact, the multistate orbital treatment[18] (Sect. 11.3a) for heavy-particle impact, or the familiar classical path and straight-line impact parameter approaches (Sect. 11.3b), which are the heavy-particle–high-energy limits of the previous semiclassical methods. The fixed-center quantal method

(Sect. 11.2b) is appropriate particularly for $nlm \rightarrow n'l'm'$ direct and rearrangement collisional transitions.

Collisional excitation involving large changes in n and ionization is best treated by the fixed-center analysis (Sect. 11.2b) and its quantal and semiquantal impulse derivatives (Sect. 11.5), which tend at high energy to the weak-coupling limit of perturbation-based procedures (such as close coupling). The semiquantal method essentially recasts the full quantal impulse treatment with a plane-wave description of the ejected electron in a form more suitable and efficient for the evaluation of A–B(n) ionization, including even ground-state targets B. For electron and ion impact, these impulse methods essentially reduce, with the use of the Rutherford cross section, to the standard binary-encounter approach[56-59] (Sect. 11.4d) with an appropriate momentum distribution for the Rydberg electron. For Rydberg collisions with ions or electrons, the $E^{-1} \ln E$ asymptotic term omitted by these impulse treatments is not important relative to the E^{-1} term but may be included by careful attention to its source (Sect. 11.5d).

Finally, classical procedures such as Monte Carlo computer simulations (Sect. 11.6) are effective for direct ionization and for charge-transfer collisions, which may also be described by the fixed-center treatment (Sect. 11.5d) and the impulse derivatives (Sect. 11.5).

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